Studies on the Ionization of Substituted Benzoic Acids

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Abstract

Titrations of 3,4-, 3,5-dimethoxy and 4-Hydroxy-3,5-dimethoxy benzoic acids have been carried out by the pH metric method, at five different temperatures from 25° to 65 °C using a Beckman pH meter. The pK values of the acids have been determined at five different temperatures. It has been observed that the substitution of a methoxy group in meta position lowers the pK value by 0.12 unit, in the para position raises the same by 0.26 unit and the substitution of a hydroxyl group in para position increases the pK value by 0.37 unit.

The influence of substituents on the ionization of benzoic acids has been a subject of several investigations[1–3]). Shorter and Stubbs[4]) have compiled the data on the subject. The data have led to the formulation of the additivity principle, which states that, in many cases the total influence on the pK value of the substituents occupying different positions in the aromatic ring is the sum of the individual contributions. The validity of this principle in the case of various acids has been shown recently[5–8]).

As a part of systematic research programme the author has determined the apparent ionization constant of 3,4-, 3,5-dimethoxy and 4-hydroxy-3,5-dimethoxy benzoic acids at various temperatures. In view of the data obtained it appeared of interest to examine the applicability of additivity principle to substituted benzoic acids. The results of these investigations are reported in the present communication.

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Experimental

3,4- and 3,5-dimethoxy benzoic acids used were of E. MERCK C.P. grade (m.p. 182°C and 186 °C; lit. val[9]) 181° and 185—186 °C. 3,4-dimethoxy benzoic acid gave methyl ester m.p. 60°, ethyl ester m.p. 43°, anhydride m.p. 125° and anilide m.p. 154 °C while 3,5-dimethoxy benzoic acid gave methyl ester m.p. 43°, ethyl ester m.p. 27°, anhydride m.p. 135° and amide m.p. 148 °C. These values were found to be in agreement with the values given in the literature[9]).

4-hydroxy-3,5-dimethoxy benzoic acid was synthesised by the method described in the literature[10]). Repeated recrystallisation from boiling double distilled water in presence of a decolourizing carbon gave a odourless product of desired purity [m.p. 207 °C lit. val[10]) 206,5 °C]. BOGERT and EHRLICH[11]) reported the m.p. as 204 °C, ALIM CHANDANI and MELDRUM[12]) as 206—207 °C and ANDERSON and NABENHAUER[13]) as 209—210 °C.

4-hydroxy-3,5-dimethoxy benzoic acid gave methyl ester hydrated m.p. 85 °C, anhydrous m.p. 108 °C, 4-ethyl ether (3,5-dimethoxy-4-ethoxy benzoic acid) m.p. 124 °C, methyl ester m.p. 65 °C ethyl ester m.p. 47° and amide m.p. 155 °C. From the amide 3,5-dimethoxy-p-phenetidine was obtained which turned blue at 190° and charred at 200 °C without melting. These values were found to be in close agreement with the values given in the literature[14]). Caustic soda used was of B.D.H. Anala R quality.

pK values of the acid at different temperatures were determined pH metrically with a BECKMAN pH meter (model G) with an extension electrode assembly. The temperature of the titration cell being maintained at the desired value of ($\pm$ 0.1 °C) by employing an oil thermostat operated by a micro relay. Nitrogen containing only 0.5% oxygen was bubbled in solutions before and during the titrations.

The apparent ionisation constant of the acid was determined by observing the change in the pH of the system. On addition of different volumes of the standard alkali solution. As in the case of various carboxylic acids a sharp inflexion was noted on the plot of pH against the volume of alkali added.

Results and Discussion

Table 1 — records the pK values of the acids at different temperatures obtained from the pH metric titration curves of the acid, these values were computed essentially by the method discussed by BRITTON[15]), the average values were obtained by the graphical procedure discussed earlier[16]). From these data the thermodynamic ionization constants of the acid corresponding to different temperatures were calculated and the data are given in column (3) Table 1.

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Table 1
Ionization constant of substituted benzoic acids at different temperatures

Temp. °C	pK	pK (Thermodynamic)
3,4-dimethoxy benzoic acid:		
25	4.35	4.36
30	4.32	4.34
40	4.28	4.30
50	4.27	4.28
60	4.24	4.25
3,5-dimethoxy benzoic acid:		
25	3.96	3.97
30	3.94	3.95
40	3.90	3.92
50	3.88	3.90
60	3.85	3.87
4-Hydroxy-3,5-dimethoxy benzoic acid:		
25	4.32	4.34
35	4.27	4.28
45	4.24	4.25
55	4.30	4.32
65	4.37	4.38

The acid strength of 4-hydroxy-3,5-dimethoxy benzoic acid is governed by methoxy and hydroxyl substituents. The methoxy group in meta position increases the acid strength because of I effect. On the other hand, the additive effect of the electron repelling nature of hydroxyl group and the electron attracting nature of carboxyl group renders the latter less ionisable when hydroxyl group occupies para position[17]).

The values for substituted benzoic acids along with the contributions of the substituents to the pK of benzoic acid[18]) are given in Table 2. These data indicate that the substitution of a methoxy group in meta position lowers the pK value by 0.12 unit, and in the para position raises the same by 0.26 unit. These considerations indicated upon application of the additivity principle, an unexpected contribution of 0.14 for methoxy substituents in 3 and 4 positions, a contribution of −0.24 for methoxy substituents in 3 and 5 positions giving a value of 4.35 and 3.97 for pK of the acid (Table 2). It has been observed that the substitution of a hydroxyl group in para position (increases the pK value by 0.37 unit) is more than that of two methoxy group in meta position giving a value of 4.34 for pK of 4-hydroxy-3,5-dimethoxy benzoic acid (Table 2).

These theoretical values are in close agreement with the value of 4.36 and 3.97 for pK of 3,4- and 3,5-dimethoxy benzoic acids obtained in the present investigation. The results obtained clearly indicate that 3,4-dimethoxy and 4-hydroxy-3,5-dimethoxy benzoic acids are weaker while 3,5-dimethoxy benzoic acid is stronger than benzoic acid.

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Table 2
pK values of substituted benzoic acids at 25 °C

Acid	pK	Contribution of Substituents
Benzoic acid	4.21	—
2-Methoxy benzoic acid	4.09	— 0.12
3-Methoxy benzoic acid	4.09	— 0.12
4-Methoxy benzoic acid	4.47	+ 0.26
3,4 Dimethoxy benzoic acid	4.36	+ 0.15
	(4.35)*)	(+ 0.14)
3,5 Dimethoxy benzoic acid	3.97	— 0.24
	(3.97)*)	(— 0.24)
4-Hydroxy-3,5-dimethoxy benzoic acid	4.34	+ 0.13

*) The theoretical values are given in parentheses.

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