The Application of the Additivity Principle to the Ionization of 2, 3- and 2, 4-Dimethoxybenzoic Acids

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The overall effect of multiple substitution in a molecule is generally the sum of the individual contributions of the substituents, and, according to Jaffé,[1] the Hammett equation can be applied to most of the cases. Exceptions to this rule have, however, been recorded,[2,3] especially when a methoxyl group is present in the system. Our findings on the ionization of 4-hydroxy 3, 5-dimethoxybenzoic acid,[4] however, strictly conform to the additivity principle. In view of the relatively few investigations reported on substituted benzoic acids, the author has determined the apparent dissociation constants of 2, 3- and 2, 4-dimethoxybenzoic acids at different temperatures. From the data obtained, it then appeared of interest to examine the applicability of the additivity principle to dimethoxybenzoic acids. The results of these investigations will be reported in the present communication.

Experimental

The 2, 3- and 2, 4-dimethoxybenzoic acids used were of E. Merck C. P. grade (m. p. 122°C and 110°C; lit.[5] 120—122°C and 109°C). The caustic soda used was of a B. D. H. AnalaR quality.

The pK values of the acid at different temperatures were determined pH-metrically with a Beckman pH meter (Model G), using an extension electrode assembly. The temperature of the titration cell was maintained at the desired value of ± 0.1°C by employing an oil thermostat operated by a micro relay.

Results and Discussion

In Table I are recorded the pK_a values of the acids at different temperatures as obtained from the pH-metric titration curves of the acid. These values were computed essentially by the method discussed by Britton[6]; the average values were obtained by the graphical procedure discussed earlier.[1] From these data the thermodynamic ionization constants of the acid corresponding to different temperatures were calculated; the data are given in column 3, Table I.

The values for methoxy-substituted benzoic acids, along with the contributions of the substituents to the pK_a of benzoic acid,[7] are recorded

Table I. The ionization constant of dimethoxybenzoic acids at different temperatures

Temp., °C	pK_a	pK_a (Thermodynamic)
2, 3-Dimethoxybenzoic acid:		
25	3.98	3.98
30	3.96	3.94
40	3.94	3.90
50	3.90	3.86
60	3.88	3.86
2, 4-Dimethoxybenzoic acid:		
25	4.36	4.36
30	4.34	4.32
40	4.30	4.28
50	4.28	4.26
60	4.25	4.24

Table II. pK_a Values of methoxy-substituted benzoic acids

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
2, 3-Dimethoxy benzoic acid	3.98	−0.23
	(3.97)*	(−0.24)
2, 4-Dimethoxy benzoic acid	4.36	+0.15
	(4.35)*	(+0.14)

* The theoretical values are given in parentheses.

1) H. H. Jaffé, *Chem. Revs.*, **53**, 243 (1953).
2) R. M. Keefer and L. J. Andrews, *J. Am. Chem. Soc.*, **78**, 5623 (1956).
3) P. J. McNulty and D. E. Pearson, ibid., **81**, 612 (1959).
4) K. C. Srivastava, *Bull. L'Academie Polonaise Des Sciences*, to be published.
5) S. I. Heilbron and H. M. Bunbury, "Dictionary of Organic Compounds," Vol. I, Eyre & Spottiswoode, London (1946), p. 881.
6) H. T. S. Britton, "Hydrogen Ions," Macmillan, London (1942).
7) J. F. J. Dippy, *Chem. Revs.*, **25**, 151 (1939).

in Table II. These data indicate that the substitution of a methoxy group in the meta position lowers the pK_a value by 0.12 unit, while that in the para position enhances the same by 0.26 unit. These considerations lead, by the application of the additivity principle, to an unexpected contribution of −0.24 for methoxy substituents in 2 and 3 positions, and to a contribution of 0.14 for methoxy substituents in 2 and 4 positions, thus giving a value of 3.97 and 4.35 for pK of the acid (Table II).

This theoretical value is in close agreement with the values of 3.98 and 4.36 for the pK_a values of 2, 3- and 2, 4-dimethoxybenzoic acids obtained in the present investigation.

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