114, would give a 99 peak. The failure to obtain a peak at 114 corresponding to a molecular weight of IV is not unexpected, as many compounds fail to give peaks corresponding to their molecular weight.

To eliminate the possibility that a thermal rearrangement of pinacol to pinacolone occurred at 185°, pinacol was heated at this temperature with 3200 p.s.i. of nitrogen in the presence of a cobalt catalyst. No rearrangement occurred, and 85%

of the starting material was recovered unchanged.

The evidence strongly indicates that acid-catalyzed reactions can occur in the system comprising synthesis gas and a cobalt catalyst at about 185°. This acid is very likely cobalt hydrocarbonyl, which is in equilibrium with dicobalt octacarbonyl
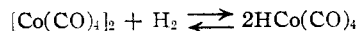
$$[Co(CO)_4]_2 + H_2 \rightleftharpoons 2HCo(CO)_4$$

Enzymatic Browning of Fruits. II. Dissociation Constants of Substituted Catechols

BY JOSEPH CORSE AND LLOYD L. INGRAHAM

The dissociation constants of several substituted catechols have been measured in aqueous dioxane solution. In the correlation of the dissociation constants by Hammett's $\rho\sigma$ treatment, better agreement was found using average values of σm and σp than by using the most acid strengthening σ.

In connection with work on the oxidation of catechols, it has been necessary to know the relative dissociation constants of certain substituted catechols. Because of the low solubility of some of the compounds in water, the dissociation constants were determined by titration with 0.1 N base in 40% dioxane (prepared by adding 400 ml. of dioxane to 600 ml. of water). The pH changes during titration were measured by means of a glass electrode which was calibrated by aqueous buffers. The values thus found in aqueous dioxane are only relative and a correction of 0.04 pK unit has been added in order to obtain the true hydrogen ion activity in 40% dioxane. This factor was evaluated by the method of Dole[2] using the vapor pressure data of Hovorka, Schaefer and Dreisbach.[3]

The pK values were calculated from the pH obtained after addition of one-half mole of base per mole of acid from the equation

$$pK = pH - \log \frac{(Na^+) + (H^+) - (OH^-)}{(Na^+) - (H^+) + (OH^-)}$$

Each pK shown in Table I represents the value obtained from a discrete titration curve. pK values above 11.4 cannot be evaluated accurately and are only reported as greater than 11.4.

Experimental

Materials.—The catechols used in this study were purified commercial chemicals or were prepared by methods described in the literature and are noted in Table I.

Titrations.—Approximately 0.4 millimole of the catechol in 40 ml. of 40% dioxane[4] was titrated with 0.1 N aqueous carbonate-free sodium hydroxide, using a 5-ml. buret. The calculated amount of pure dioxane was added to the catechol solution at the beginning of the titration to obtain a 40% dioxane solution at the half-equivalence point. The pH was determined with a glass electrode and a Beckman model G

pH meter. At pH values greater than 10.5 a "blue type E" Beckman glass electrode was used. The glass electrodes were standardized against 0.05 N potassium acid phthalate (pH assumed to be 4.00 at 25.0°). The titration vessel was jacketed with water at 25.0°, and nitrogen purified with Fieser's solution[5] was passed through the titration cell to prevent oxidation. The nitrogen rate of flow was such that if it were stopped no noticeable change was observed on the pH meter. With the type E glass electrode the flow had to be stopped entirely to obtain a reading.

Discussion

An attempt was made to relate the dissociation constants by Hammett's[6] $\rho\sigma$ treatment for those substituents whose σ values are known. However, since a substituent in a 4-substituted catechol is both meta and para to a phenolic hydroxyl group, it is not immediately apparent which value (σ_m or σ_p) should be used to calculate the dissociation. An initial assumption is to use the most acid strengthening (higher) σ value; this assumes that the corresponding hydrogen ionizes and that the other hydroxy group (ortho to the ionized group) remains a constant factor throughout the series. For catechol itself, we no longer know which hydrogen leaves, and the dissociation constant must be corrected by a statistical factor of 2.

The data treated in this manner are shown in Fig. 1. The least squares line through these points gives $pK_0 = 11.12$, $\rho = 2.703$ and a standard error[7] of 0.16 in pK.

A better fit is obtained if an average value of σ_m and σ_p is used. This treatment is shown in Fig. 2. The least squares line in this case gives $pK_0 = 10.84$, $\rho = 3.299$ and a standard error in pK of 0.07. This treatment probably owes its success to the fact that the intramolecular hydrogen bonding in the catechol causes strong interaction between the oxygens. A substituent affecting the charge on one oxygen must also affect the other oxygen. The loss of either proton must give the same ion.

It is fully realized that with a substituent the

(1) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

(2) Malcolm Dole, "The Glass Electrode," John Wiley and Sons, Inc., New York, N. Y., 1941, p. 276.

(3) F. Hovorka, R. A. Schaefer and O. Dreisbach, THIS JOURNAL, 58, 2264 (1936).

(4) Purified by the method described in L. F. Fieser, "Experiments in Organic Chemistry," 2nd Ed., D. C. Heath and Co., New York, N. Y., 1941, p. 368.

(5) Reference 4, p. 395.

(6) L. P. Hammett, "Physical Organic Chemistry," Chapter VII, McGraw-Hill Book Co., Inc., New York, N. Y., 1940.

(7) F. C. Mills, "Statistical Methods," Henry Holt and Company, New York, N. Y., 1940, p. 330.

TABLE I

pK's IN 40% DIOXANE

Compound	pK	Equivalent weight Calcd.	Found
Tetrachlorocatechol[b]	6.63,6.61,6.64	248	249
3-Nitrocatechol[c]	7.51,7.56,7.57,7.54,7.55	155	155
4-Nitrocatechol[c]	7.65,7.65,7.66	155	155
4-Formylcatechol (protocatechualdehyde)[d]	8.32,8.30,8.24	138	137
4-Chloroacetylcatechol[e]	8.52,8.55,8.55	187	191
3,4-Dihydroxybenzophenone[f]	8.84,8.79,8.82	214	220
3,4-Dihydroxyacetophenone[f]	8.89,8.89,8.88,8.88	152	154
3-Bromocatechol[g]	9.41,9.39,9.39	189	185
3-Fluorocatechol[h]	9.78,9.76,9.79	128	131
4-Bromocatechol[i]	9.85,9.80	189	186
Chlorogenic acid ($^i pK_2$) (hemihydrate)	9.84,9.87,9.82	363	362
4-Chlorocatechol[k]	9.89,9.94,9.94	145	149
4-Fluorocatechol[h]	10.04,10.09,10.09	128	126
3,3',4,4'-Tetrahydroxybiphenyl[a,l]	10.29,10.35	218	...
Caffeic acid $(pK_2)^m$	10.57,10.49,10.54	180	184
3,4-Dihydroxybiphenyl[a,b]	10.71,10.74,10.74,10.77	186	...
Catechol[b]	10.87,10.88,10.91,10.93	110	108
4-Methoxycatechol[n]	11.01,11.02,11.03	140	...
3-Methylcatechol[a,o]	11.11,11.06	124	...
3-Methoxycatechol[a,p]	11.16,11.20,11.19	140	...
4-Methylcatechol[a,q]	11.31,11.28,11.33	124	...
Protocatechuic acid[a,r] (pK_2) (monohydrate)	>11.4	172	170
4-t-Butylcatechol[a,b]	>11.4	166	...
4,6-Di-t-butylcatechol[a,s]	>11.4	222	...
2,3-Dihydroxybenzoic acid[a,t] (pK_2) (hemihydrate)	>11.4	163	167

[a] No phenolic inflection was observed at the equivalence point. [b] Recrystallized Eastman Kodak Co. product. [c] D. H. R. Barton, W. H. Linnell and N. Senior, *Quart. J. Pharm. and Pharmacol.*, **18**, 41 (1945). [d] J. S. Buck and F. J. Zimmermann, "Organic Syntheses" Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 549. [e] H. D. Hobermann, THIS JOURNAL, **57**, 1382 (1935). [f] K. W. Rosenmund and H. Lohfert, *Ber.*, **61**, 2601 (1928). [g] H. S. Mason, THIS JOURNAL, **69**, 2241 (1947). [h] J. Corse and L. L. Ingraham, *J. Org. Chem.*, in press. [i] H. D. Dakin, *Am. Chem. J.*, **42**, 477 (1909). [j] R. G. Moores, D. L. McDermott and T. R. Wood, *Anal. Chem.*, **20**, 620 (1948). [k] R. Willstätter and H. E. Müller, *Ber.*, **44**, 2182 (1911). [l] E. Späth and K. Gibian, *Monatsh.*, **55**, 342 (1930). [m] F. Vorsatz, *J. prakt. Chem.*, **145**, 265 (1936). [n] D. E. Kvalnes, THIS JOURNAL, **56**, 2487 (1934). [o] R. Majima and Y. Okazaki, *Ber.*, **49**, 1489 (1916). [p] A. R. Surrey, *Org. Syntheses*, **26**, 90 (1946). [q] Hydrobromic acid hydrolysis of 2-methoxy-4-methylphenol (Eastman Kodak Co.). [r] I. A. Pearl, *Org. Syntheses*, **29**, 85 (1949). [s] E. R. Erickson, British Patent 596,461 (*C. A.*, **42**, 5470 (1948)). [t] E. Späth and H. Holter, *Ber.*, **60**, 1897 (1927).

oxygens do not have the same electronegativity and perhaps some weighted average of σ values would be better. The precision of our data is not great enough to determine what weighting factor should be used.

The high values of ρ found in both treatments is in keeping with the results of other similar reactions where atoms directly attached to the benzene ring are involved.

The results for 3,4-dihydroxybiphenyl were anomalous in both methods of treatment of the data. This may be due to the large errors in the
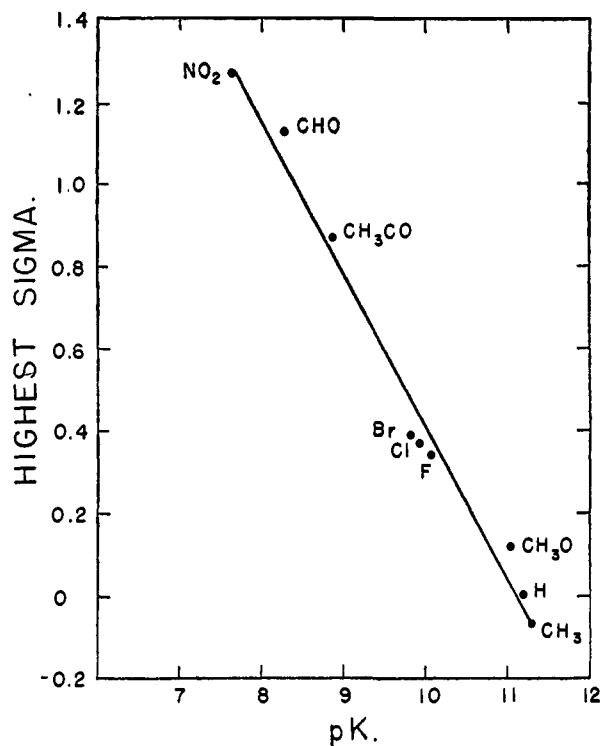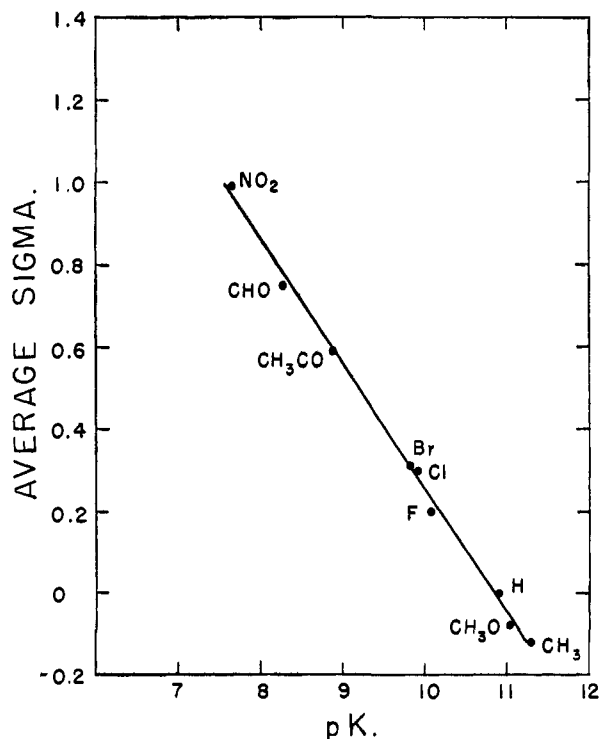

Fig. 1.

Fig. 2.

values of sigma for a phenyl group.[6] The pK for 3,4-dihydroxybiphenyl was not included in either least squares treatment.

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