Iron(III)–Phenol Complexes. II. Iron(III) and Proton Associations with Some Singly Substituted Phenolate Ions at 25°[1,2]

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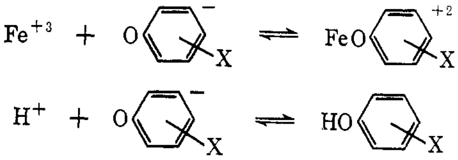
Abstract: Potentiometric methods have been used to obtain equilibrium quotients at 25° for the association reactions (1) $Fe^{+3} + OC_6H_4X^- \rightleftarrows FeOC_6H_4X^{+2}$ and (2) $H^+ + OC_6H_4X^- \rightleftarrows HOC_6H_4X$, with X equal to *o*-$NO_2$, *m*-$NO_2$, *p*-$NO_2$, *o*-F, *m*-F, *p*-F, *o*-Cl, *m*-Cl, *p*-Cl, *o*-Br, *m*-Br, *p*-Br, and *m*-I. The medium was aqueous 0.10 *M* perchlorate ($NaClO_4$–$HClO_4$). Within the limits of experimental error, the distribution of points in a plot of log K_X against log K_H is summarized satisfactorily by a single line of unit slope. The dangers in utilizing linear free-energy plots and deviations from such plots to draw conclusions about bonding differences between corresponding metal–ligand and proton–ligand complexes are analyzed.

In an earlier study[3] in which the stabilities of 1:1 iron(III)–phenolate complexes were measured in aqueous solution for phenol and several singly substituted *para* and *meta* derivatives, an approximately linear relation was observed between the free energies for the association reactions


(1)

(2)

Small deviations from linearity were observed, and it was suggested that the two sets of reactions might have nonparallel entropy dependencies and/or that there might be double-bond character to the iron(III)–phenolate bonds. The present paper and one to follow[4] describe additional investigations, covering a selection of closely related phenols, which have been made to specify more precisely the factors determining the relative stabilities of iron(III) and proton–phenolate complexes.

This report describes the development and use of an emf method for measurement of equilibrium quotients for the formation of iron(III)–phenolate complexes. Evidence is presented for a relatively good linear relation between the free energies of reactions 1 and 2 for the 13 substituents examined. Discussion emphasizes the implications of these results and the difficulties in utilizing "linear free-energy plots" (including deviations from such plots) to draw conclusions about π bonding in metal complexes.

Experimental Section

Reaction Conditions. In all cases the medium was aqueous 0.10 *M* perchlorate ($NaClO_4/HClO_4$), and the temperature was maintained at 25.0 ± 0.1°.

Materials. Water was purified by heating ordinary distilled water with potassium permanganate and sodium hydroxide and redistilling in a Barnstead S-1 apparatus. This water was freshly boiled and cooled before use. Standard perchloric acid and sodium perchlorate solutions, prepared as previously described,[5] were used for the adjustment of hydrogen ion concentration and ionic strength. The solutions gave negative tests for chloride and for iron(III) ions. A stock iron(III) perchlorate solution was prepared also as previously described.[5] Iron(II) perchlorate solutions were prepared fresh, as required, from perchloric acid and iron wire of established purity. Iron(II) solutions, and iron(III) solutions after reduction in a Jones reductor, were analyzed by titration with standardized fresh potassium permanganate solutions. The perchloric acid content was determined for the iron(III) perchlorate solution as before,[5] and for the iron(II) perchlorate solution from the iron(II) concentration and the known amount of acid used to dissolve the iron wire. The phenols were the purest samples obtainable. Further purification was achieved by recrystallization (from chloroform or water where possible), or by distillation under low pressure. The purity of each phenol was checked by determining the melting point and/or by running vapor phase chromatograms in benzene. Sodium hydroxide solutions, used in the potentiometric titration of the phenols, were prepared by the method of Allen and Low.[6] The absence of carbonate from these solutions was established and periodically checked by titration with hydrochloric acid, using first phenolphthalein and then methyl orange.

Proton–Phenolate Associations. Equilibrium quotients for reactions of type 2 (K_H values) were determined by the Bjerrum–Calvin pH titration technique as adapted by Irving and Rossotti.[7] The pH readings were taken with a Radiometer pH Meter 4 used in conjunction with Radiometer G2025B glass and K4025 reference calomel electrodes. For calibration three buffers were used: 0.05 *m* potassium hydrogen phthalate (pH 4.01), 0.01 *m* borax buffer (pH 9.18), and in certain cases 0.05 *m* potassium tetroxalate (pH 1.68). Before and after each titration, the instrument was calibrated with one buffer and immediately checked against another. Results were considered to be acceptable where buffer readings, before and after the titration, were in agreement to within ±0.01 pH unit. Prior to each series of measurements, an approximately 1 *M* NaOH solution was freshly prepared from stock ~20 *M* alkali and was standardized by potentiometric titration against a standard potassium acid phthalate solution. In a typical pK_a determination the standardized ~1 *M* NaOH (in a calibrated 2-ml buret) was used to titrate first 40 ml of a solution containing 0.80 mmole of $HClO_4$ and 3.2 mmoles of $NaClO_4$, and then, immediately afterward, a solution which was identical except for the inclusion of ~0.4 mmole of the phenol. Each such set of two titrations was performed in duplicate with use of different glass electrodes for the two sets. During the titrations, a slow stream of prepurified and medium-saturated N_2 was bubbled through the solution.

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[1] Supported by Research Grant GM-07493 from the National Institute of General Medical Sciences, Public Health Service.

[2] Presented in part at the Eighth International Conference on Coordination Chemistry, Vienna, Sept 1964.

[3] R. M. Milburn, *J. Am. Chem. Soc.*, 77, 2064 (1955) (to be considered part I of this series).

[4] R. M. Milburn, Part III, "Enthalpies and Entropies of Iron(III)–Phenolate Associations," to be published.

[5] R. M. Milburn and W. C. Vosburgh, *J. Am. Chem. Soc.*, 77, 1352 (1955).

[6] N. Allen and G. W. Low, *Ind. Eng. Chem., Anal. Ed.*, 5, 192 (1933).

[7] H. M. Irving and H. S. Rossotti, *J. Chem. Soc.*, 2904 (1954).

In accord with established computational technique,[7,8] $\bar{n}_A$ values were obtained from the two titration curves at the same pH values with use of the equation

$$\bar{n}_A = \left\{ yT_L^0 + \frac{(v' - v'')(N + E^0)}{(V^0 + v')} \right\} / T_L^0 \qquad (3)$$

where the symbols are used in their previous sense[7] (thus T_L^0 is the total phenol concentration, y is the number of titratable hydrogens in the reagent molecule and is thus here equal to 1, N is the concentration of NaOH being added, E^0 is the initial concentration of $HClO_4$, V^0 is the initial volume of the solution, and v' and v'' are the volumes of alkali needed to reach the same pH values in the two titrations). Values of K_H were then calculated from the various $\bar{n}_A$ values from

$$K_H = \left(\frac{\bar{n}_A}{1 - \bar{n}_A} \right) / [H^+] \qquad (4)$$

where $[H^+]$ values were obtained from the measured pH from

$$pH_{meas} = p[H^+] - \log f \qquad (5)$$

with the activity coefficient term calculated by the Davies equation[9]

$$-\log f = 0.50Z^2 \left(\frac{\mu^{1/2}}{1 + \mu^{1/2}} - 0.30\mu \right) \qquad (6)$$

Such a procedure adopts the usual operational definition of pH and makes the reasonable assumption that, for the pH range of the measurements, the liquid junction potentials of buffer and test solutions will be closely matched.[10]

The following data obtained for *p*-fluorophenol are typical. Numbers in each set refer to pH_{meas}, $p[H^+]$, $\bar{n}_A$, and $K_H \times 10^{-9}$ respectively: 8.90, 8.79, 0.826, 2.93; 9.00, 8.89, 0.786, 2.85; 9.10, 8.99, 0.740, 2.78; 9.20, 9.09, 0.696, 2.82; 9.30, 9.19, 0.648, 2.85; 9.40, 9.29, 0.599, 2.91; 9.50, 9.39, 0.541, 2.89; 9.60, 9.49, 0.486, 2.92; 9.70, 9.59, 0.430, 2.94; 9.80, 9.69, 0.376, 2.95; 9.90, 9.79, 0.321, 2.92; 10.00, 9.89, 0.272, 2.90; 10.10, 9.99, 0.225, 2.84; 10.20, 10.09, 0.187, 2.83; 10.30, 10.19, 0.151, 2.75. Hence $K_H = 2.87 (\pm 0.06) \times 10^9$.

Resulting log K_H values are: *o*-NO_2, 7.04; *m*-NO_2, 8.04; *p*-NO_2, 7.02; *o*-F, 8.49; *m*-F, 8.81; *p*-F, 9.46; *o*-Cl, 8.33; *m*-Cl, 8.76; *p*-Cl, 9.10; *o*-Br, 8.22; *m*-Br, 8.75; *p*-Br, 9.06; *m*-I, 8.74. Standard deviations calculated for individual values are of the order ±0.02 unit; uncertainties in absolute values are of the order ±0.1 unit.[11] The values, when extrapolated to zero ionic strength with use of eq 6, compare fairly satisfactorily with the thermodynamic constants of Biggs and Robinson,[12] the mean deviation for the 13 phenols being 0.09 log unit.

Iron(III)–Phenolate Associations. For reactions of type 1, equilibrium quotients (K_X) were determined from measurement of iron(III) ion and hydrogen ion concentrations with use of the cell systems

$$\begin{array}{c|c|c|c} \text{calomel} & \text{satd} & Fe^{+2}, Fe^{+3}, XC_6H_4OH & \text{Pt or glass} \\ \text{electrode} & \text{KCl} & H^+, Na^+, ClO_4^- & \text{electrode} \end{array}$$

A Leeds and Northrup Universal potentiometer 7553, Type K-3, with a stabilized dc microvolt amplifier 9835 by the same manufacturer, was used for emf measurements.

Series of solutions containing varying proportions of $HClO_4$ and $NaClO_4$ were prepared with constant total iron(III), iron(II), and phenol concentrations. As before, the total perchlorate concentration was held at 0.10 *M*. The total iron(III) concentration, $[Fe^{+3}]_t$, was equal to or slightly less than 10^{-3} *M*, while the hydrogen ion concentration was kept $>4 \times 10^{-3}$ *M*. About 12 hr before each series of measurements, an iron(II)–iron(III) solution (~0.03 *M* in total iron and ~0.06 *M* in $HClO_4$) was prepared from stock solutions of iron(III) and iron(II). Shortly before the measurement, aliquots of this solution were diluted with appropriate volumes of standard $NaClO_4$ solutions and either water (for study of the hydrolysis of iron(III)) or aqueous phenol. The electrodes were immediately introduced into these solutions and cell emf values were measured after about 3 min, and thereafter every several minutes for some 10 to 15 min. For the particular phenols studied, the cell emf's over this period of time were constant to 0.1 mv for the Pt electrode and to 0.002 pH unit for the glass electrode. By this technique it was possible to avoid difficulties which could otherwise arise from oxidation–reduction instabilities of certain of the iron(III) complexes, leakage of Cl^- into the test solutions, and deposition of $KClO_4$ in the vicinity of the liquid junction.

The hydrolysis of iron(III) was first examined for the particular conditions. In the absence of phenol, the total iron(III) concentration was identified with $[Fe^{+3}] + [FeOH^{+2}]$. Evidence exists in support of the view that as a good approximation hydrolyzed products other than $FeOH^{+2}$ can be neglected for the chosen reaction conditions. Thus, our earlier spectrophotometric studies have shown that polymeric hydrolyzed iron(III) species will here be of little importance,[3,5] and it has been further indicated that $Fe(OH)_2^+$ will be unimportant as demonstrated by linearity in plots of $1/A$ *vs.* $[H^+]$ and by the existence of sharp isosbestic points at 273 mμ[5] and 225 mμ.[13] It is relevant to note that an analogous position has been taken by King, *et al.*,[14] in treatment of the iron(III)–chloride system for which it is argued that $k_1 >> k_2$.

In the absence of phenol we then write for the total iron(III) concentration

$$[Fe^{+3}]_t = [Fe^{+3}] + [FeOH^{+2}] \qquad (7)$$

Also, for the pH range of the investigation, iron(II) shows no tendency to hydrolyze.[15] Thus, in the case where activity coefficients and the liquid junction potential may be considered to be constant, one may write for the oxidation–reduction potential

$$\frac{E_0' - E}{0.059158} = \log \frac{[Fe^{+3}]_t}{[Fe^{+3}]} \qquad (8)$$

where E_0' is the potential (in volts) the cell would have if *none* of the iron(III) were hydrolyzed. A first estimate of E_0' may be obtained from the cell potential with 0.100 *M* $HClO_4$ as electrolyte. Use of this first estimate together with the measured E through the pH_{meas} range ~2.0–2.4, where iron(III) is more significantly hydrolyzed, then allows calculation of a value for the first hydrolysis equilibrium quotient, k_1 ($=[FeOH^{+2}][H^+]/[Fe^{+3}]$), for various hydrogen ion concentrations from eq 8 and 9.

$$\frac{[Fe^{+3}]_t}{[Fe^{+3}]} - 1 = \frac{k_1}{[H^+]} \qquad (9)$$

Such calculated k_1 values exhibit a marked trend with hydrogen ion concentration. We attribute this difficulty largely to an improper E_0' value[16] which arises because: (1) a small fraction of the iron(III) (about 3%) remains hydrolyzed in 0.100 *M* $HClO_4$; (2) the same liquid junction potential will not pertain for 0.100 *M* $HClO_4$ and for the solutions covering the narrow pH range ~2.0–2.4 through which E_j *can* be taken to be essentially constant;[17–19] (3) the activity coefficients of relevant species (Fe^{+3}, $FeOH^{+2}$, H^+, and Fe^{+2}) will not be the same in 0.100 *M* $HClO_4$ and in the solutions of lower acidity.[20] When E_0' is taken to be 3.3 mv greater than the E measured for 0.100 *M* $HClO_4$, the k_1 calculated from the E values

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[8] K. E. Jabalpurwala, K. A. Venkatachalam, and M. B. Kabadi, *J. Inorg. Nucl. Chem.*, **26**, 1011 (1964).

[9] C. W. Davies, "Ion Association," Butterworths, London, 1962, p 41.

[10] R. G. Bates, "Reference Electrodes," D. J. G. Ives and G. J. Janz, Ed., Academic Press Inc., New York, N. Y., 1961, p 239.

[11] Because of modified calculational procedures, all constants reported in the present paper differ slightly from the values given earlier.[2] Equilibrium quotients for *o*- and *p*-iodophenol have not been included because of uncertainties arising from the oxidation–reduction instabilities of the iron(III) complexes.

[12] (a) A. I. Biggs and R. A. Robinson, *J. Chem. Soc.*, 388 (1961); (b) A. I. Biggs, *Trans. Faraday Soc.*, **52**, 35 (1956).

[13] R. C. Turner and K. E. Miles, *Can. J. Chem.*, **35**, 1002 (1957).

[14] M. J. M. Woods, P. K. Gallagher, and E. L. King, *Inorg. Chem.*, **1**, 55 (1962).

[15] B. O. A. Hedström, *Arkiv Kemi*, **5**, 457 (1953).

[16] As implied above, the data might be interpreted alternatively on the basis that $Fe(OH)_2^+$ is also of importance. Of course, resolution of the data to provide the proper k_1 and k_2 values still requires knowledge of the correct E_0'. We take the view that k_1 will be large in comparison to k_2, however, because of the linearity in plots of $1/A$ *vs.* $[H^+]$ and because of the existence of the isosbestic points.

[17] G. G. Manov, N. J. Delollis, and S. F. Acree, *J. Res. Natl. Bur. Std.*, **34**, 115 (1945).

[18] G. Biedermann and L. G. Sillén, *Arkiv Kemi*, **5**, 425 (1953).

[19] R. G. Bates, "Determination of pH, Theory and Practice," John Wiley and Sons, Inc., New York, N. Y., 1964, p 41.

[20] See, for example, R. N. Heistand and A. Clearfield, *J. Am. Chem. Soc.*, **85**, 2566 (1963).

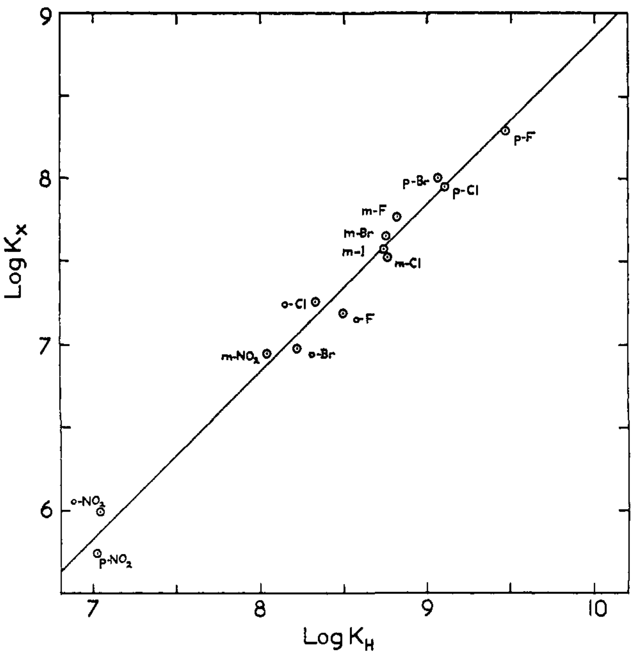

Figure 1. Equilibrium quotients for reactions 1 and 2 (25°, ionic strength = 0.10). The least-squares line is shown, with slope equal to 1.01 and standard deviation in the slope equal to 0.04.

through the pH_{meas} range ~2.0–2.4 is in accord with the value appropriate for the conditions as obtained earlier by spectrophotometry ($k_1 = 2.89 \times 10^{-3}$)[5]. Thus, adoption of this E_0' gives the following results,[21] where pairs of values refer to pH_{meas} and k_1, respectively: 2.070, 2.80×10^{-3}; 2.125, 2.80×10^{-3}; 2.181, 2.87×10^{-3}; 2.235, 2.95×10^{-3}; 2.313, 3.07×10^{-3}. Average $k_1 = 2.90 \times 10^{-3}$.

Similar potentiometric measurements were now made on solutions which also contained the phenol in order to obtain first phenolysis constants, k_x, referring to reactions of type 10.

(10)

For each phenol the first estimate of E_0' was obtained, as before' with use of 0.100 *M* $HClO_4$ as medium. The difference between this estimate and the proper E_0' was taken to be the same as that necessary to bring the emf and spectrophotometric studies of the hydrolysis reaction into coincidence (*i.e.*, 3.3 mv). Such a procedure is based on the reasonable assumption that the low phenol concentrations used (~0.01 *M*) will have negligible influence on the liquid junction potential and on the activity coefficients of relevant species.[22] Values of $[Fe^{+3}]$ were then obtained from eq 8, and these were introduced together with $k_1 = 2.89 \times 10^{-3}$ into eq 11 for the evaluation of k_x.[23]

$$\frac{[Fe^{+3}]_t}{[Fe^{+3}]} - 1 - \frac{k_1}{[H^+]} = \frac{k_x[XC_6H_4OH]}{[H^+]} \qquad (11)$$

The following results for *m*-bromophenol are typical, where pairs of values refer to pH_{meas} and k_x, respectively: 2.087, 0.073; 2.155, 0.069; 2.210, 0.085; 2.301, 0.082; 2.351, 0.086. Average k_x = 0.079.

Resulting values of $-\log k_x$ are: *o*-NO_2, 1.05; *m*-NO_2, 1.09; *p*-NO_2, 1.28; *o*-F, 1.30; *m*-F, 1.04; *p*-F, 1.17; *o*-Cl, 1.07; *m*-Cl, 1.24; *p*-Cl, 1.15; *o*-Br, 1.24; *m*-Br, 1.10; *p*-Br, 1.06; *m*-I, 1.17. Values of $\log K_x$ ($= \log \{k_x K_H\}$) are: *o*-NO_2, 5.99; *m*-NO_2, 6.95; *p*-NO_2, 5.74; *o*-F, 7.19; *m*-F, 7.77; *p*-F, 8.29; *o*-Cl, 7.26; *m*-Cl, 7.52; *p*-Cl, 7.95; *o*-Br, 6.98; *m*-Br, 7.65; *p*-Br, 8.00; *m*-I, 7.57.

Discussion

The resulting equilibrium quotients for reactions of types 1 and 2 are compared in Figure 1. Uncertainties in the $\log K_H$ values are of the order ±0.1 unit, and uncertainties in the relative $\log K_x$ values are of the order ±0.15 unit. Within these limits the points fall on a straight line of unit slope (the least-squares slope is 1.01 with a standard deviation of 0.04).

Assessment of absolute uncertainties in the $\log K_x$ values is more difficult. The choice of k_1 and E_0' has little effect on the relative values of $\log K_x$, but use of somewhat different k_1 and E_0' values markedly influences the absolute values of the various $\log K_x$. Thus an increase of E_0' by 1 mv (maintaining the accepted value of k_1) or a decrease in k_1 by 15–20% (maintaining the accepted value of E_0') results in ~100% increase in the k_x values (*i.e.*, increases in the $\log k_x$ or $\log K_x$ values by ~0.3 unit). Comparison of values with those obtained by spectrophotometry[3,24] requires consideration of quotients which apply to the same set of conditions. Extrapolation of the present k_x values to zero ionic strength, taking the ionic strength dependence of the constants to be the same as that observed for the first hydrolysis constant,[5] and use of the $K_H{}^0$ values of Biggs and Robinson[12] (these being used by Ernst and Herring[24]) produces $\log K_x{}^0$ values which are consistently higher than the spectrophotometric values by about 0.5 log unit. Thus for *p*-NO_2, *m*-NO_2, and *p*-Br, previously examined by Milburn,[3] respective differences are 0.50, 0.44, and 0.59 log unit; for *o*-F, *m*-F, *p*-F, *o*-Cl, *m*-Cl, *p*-Cl, and *o*-Br examined by Ernst and Herring, respective differences are 0.45, 0.77, 0.73, 0.51, 0.37, 0.72, and 0.38 unit. The differences do not necessarily imply a constant error in the potentiometric values. The spectrophotometrically obtained k_x values are also liable to significant errors since the observed magnitudes of the quotients are extremely dependent on the value used for the hydrolysis quotient and on the remainder of the procedure which results in resolution of measured absorbances into absorbancy coefficients and concentrations of complex.[25] In addition, lengthy extrapolations required in order to compare quotients for identical conditions could lead to the introduction of significant errors. Possibly, for example, reaction 10 and the corresponding first hydrolysis reaction are influenced rather differently by changes in ionic strength ($FeOC_6H_4X^{+2}$ ions could be more strongly polarized and/or more readily polarizable than $FeOH^{+2}$). Again, neg-

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[21] The pH range is necessarily narrow because of the increased importance of other hydrolysis (and phenolysis) products at higher pH, and the lack of importance of the first hydrolysis product (and the first phenolysis product) at lower pH. The range corresponds to that utilized for the study of the phenol complexes. A major part of the residual trend in k_1 with pH can be accounted for[5] by increased importance of $Fe_2(OH)_2{}^{+4}$ at higher pH, but we have not deemed it necessary, in the present study, to correct for this small effect.

[22] Refined calculations for the 0.100 *M* $HClO_4$ medium, taking into account the difference in the free iron(III) ion concentration in the absence and in the presence of phenol, have no significant effect on E_0'.

[23] A value of k_x can be obtained first using the stoichiometric concentration of XC_6H_4OH in eq 11. This k_x value then allows estimation of the equilibrium concentration of phenol, $[XC_6H_4OH]$, for a second calculation of k_x. In practice, for the concentrations of iron(III) and phenol used, the two values of k_x were in all cases almost identical and certainly within the limits of experimental error.

[24] Z. L. Ernst and F. G. Herring, *Trans. Faraday Soc.*, **61**, 454 (1965).

[25] While the apparent agreement between the two spectrophotometrically obtained sets of data is good as shown by a $\log K_x{}^0$ *vs.* $\log K_H{}^0$ plot in which the points are accommodated by a single line,[24] a cross check on the reliability of individual constants within the two sets is not possible since in no case was the same phenol included in both investigations. For each of these two spectrophotometric studies, as has been pointed out,[3,24] the $\log K_x{}^0$ *vs.* $\log K_H{}^0$ comparison reveals considerable scatter. It has been supposed that this scatter is in excess of that arising from experimental error.

lect of dimerization of $FeOH^{+2}$ in the present and earlier studies of the phenolate complexes is an approximation which might bear careful reexamination.

It is likely that further investigation of these iron(III)–phenol systems using solutions more dilute in iron(III), with systematic variations in total metal and total phenol concentrations and in ionic strength, will lead to more reliable estimates for the absolute magnitudes of the quotients. For the present, however, the significant features are the relative values of the quotients, and in particular the *linearity* in the log K_x *vs.* log K_H plot and the *unity* of the slope.

The absence of serious scatter for *ortho*-substituted phenols, as shown by the results in Figure 1 and by the work of Ernst and Herring,[24] indicates that any special interactions of the iron(III) with the chosen *ortho* substituents are effectively balanced by proton-substituent interactions in the free phenol. That the iron(III) complex of *o*-nitrophenol is of normal stability is of interest in that spectral methods have not here been of use in detecting complex formation.

Linear free-energy relationships of the type shown by Figure 1 for the *meta*- and *para*-substituted ligands, and especially the slopes of the lines and the deviations of points from the lines, have sometimes been used as a measure of π bonding in the metal complexes. Thus, Williams, *et al.*,[26] have interpreted our earlier spectrophotometric results[3] as indicating that *p*-bromo and *p*-methyl stabilize and *p*-nitro destabilizes the iron(III)–phenolates relative to the free phenols. This interpretation is in accord with the view that the iron(III) acts as a *π-electron acceptor.*[26] It may be noted that the present results indicate that while *p*-bromo lies above and *p*-nitro lies below the unit slope line, the deviations are within the limits of experimental error in the relative values. On the other hand, Ernst and Herring[24] find their log K_x *vs.* log K_H plot (which includes our earlier spectrophotometric results) has a slope of 0.8 with a standard deviation of ±0.3, and it is concluded that the iron(III) is behaving in the phenolate complexes as a *π-electron donor.* The magnitude of the standard deviation would, in itself, lead one to question this controversial interpretation of the bond character.

It is by no means apparent, even where experimental precision is not a limiting factor, that such free-energy plots should reflect differences between corresponding metal–ligand and proton–ligand bonds. The special circumstances required in order that the free-energy plots should indicate bonding differences can be specified by reference to the exchange reactions

$$FeOC_6H_5^{+2} + OC_6H_4X^- \rightleftharpoons OC_6H_5^- + FeOC_6H_4X^{+2} \quad (12)$$

$$HOC_6H_5 + OC_6H_4X^- \rightleftharpoons OC_6H_5^- + HOC_6H_4X \quad (13)$$

For any reaction of type 12 or 13 we may write, in accordance with Hepler[27]

$$\Delta F = \Delta H_{int} + \Delta H_{ext} - T(\Delta S_{int} + \Delta S_{ext}) \quad (14)$$

where subscripts refer to "internal" contributions arising within the reactant species (the identities of which may be specified by the chemical equations, or otherwise) and to "external" contributions associated with solute–solvent interaction. Now, a unit-slope line in a plot of ΔF values between reactions 1 and 2 is equivalent to a unit-slope line passing through the origin in a plot of ΔF values between reactions 12 and 13. To be able to equate deviations from linearity or from unity of slope in the ΔF plots (for reactions 1 and 2, or 12 and 13) to differences which substituents X cause in the internal bond energies for the iron(III) and proton complexes, there would have to be a direct proportionality of $(\Delta H_{ext} - T\Delta S)$ between reactions 12 and 13. For reactions of type 13 it has been argued[27] that ΔH_{ext} will be proportional to ΔS ($= \Delta S_{ext}$, since $\Delta S_{int} \sim 0$), and on similar grounds one might anticipate a proportionality between ΔH_{ext} and ΔS for reactions of type 12. The requirement of proportionality of $(\Delta H_{ext} - T\Delta S)$ between the reaction sets could thus reduce to proportionality between the ΔS values.

Some have taken the view that the entropy changes for reactions of type 1 will be insensitive to the identity of X in *meta* and *para* positions; similarly for reactions of type 2. Such a position amounts to the assumption that ΔS for the reactions of types 12 and 13 will be essentially zero. That this is far from the case for phenolic acid dissociations is shown by the work of Hepler and co-workers.[27–29] We shall shortly report[4] on the extreme importance of entropy considerations for reactions of types 1 and 12.

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(26) J. G. Jones, J. B. Poole, J. C. Tomkinson, and R. J. P. Williams, *J. Chem. Soc.*, 2001 (1958).

(27) L. G. Hepler, *J. Am. Chem. Soc.*, **85**, 3089 (1963).

(28) L. P. Fernandez and L. G. Hepler, *ibid.*, **81**, 1783 (1959).

(29) H. C. Ko, W. F. O'Hara, T. Hu, and L. G. Hepler, *ibid.*, **86**, 1003 (1964).