

Iron(III)–Phenol Complexes. IV. Further Thermodynamic Studies of Iron(III)–Phenolate and Proton–Phenolate Associations¹

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Abstract: Free-energy, enthalpy, and entropy changes have been measured at ionic strength 0.10 for reactions of the types $\text{Fe}^{3+} + \text{OC}_6\text{H}_4\text{X}^- \rightleftharpoons \text{FeOC}_6\text{H}_4\text{X}^{2+}$ (1) and $\text{H}^+ + \text{OC}_6\text{H}_4\text{X}^- \rightleftharpoons \text{HOC}_6\text{H}_4\text{X}$ (2), with X = H, *p*-NO₂, *m*-NO₂, *p*-CN, *m*-CN, *o*-CN, *p*-Cl, *m*-Cl, *o*-Cl, and *p*-CHO. Improved methods have been used to measure the thermodynamic values for reactions 1 which include use of iron(III) concentrations as low as $2 \times 10^{-4} M$ to minimize the importance of polynuclear species. Apart from *o*-cyanophenolate ion, which forms a disproportionately strong complex with iron(III), a linear free-energy relation of unit slope is observed between reactions of types 1 and 2. For these reactions additional support is given to the previously expressed view that changes in free energy with substituent ($\delta\Delta G$ values) are a fair measure of relative changes in internal bond energies because of approximate cancellations of corresponding $\delta\Delta H_{\text{ext}}$ and $-T\delta\Delta S$ values.

In our earlier studies of the influences of aromatic substituents X on reactions of the types



a linear free-energy relation of unit slope was observed between the two reaction types.^{2,3} The most recent of these reports³ illustrated the extreme importance of entropy factors in determining both the individual and relative stabilities of the various iron(III)–phenolate complexes. These results were clear-cut. Nevertheless, as we have been careful to point out,³ some less than completely satisfactory features remained, which placed larger uncertainties in absolute values than one would have liked. Further, the earlier temperature-dependent study had been confined to just four phenols. We have now adjusted our experimental procedure to provide increased reliability in the data and have extended the temperature-dependent measurements to include a larger range of substituents.

The procedure used to obtain the previously reported data involved (a) direct determination of equilibrium quotients (k_x) for reactions of type 3 for temperatures close to 25°;^{2,3} (b) measurement of the temperature



dependence of k_x values by a method which avoided uncertainties which would be associated with the independent determination of the k_x for each of the temperatures examined;³ (c) measurement of equilibrium quotients for reactions of type 2 (K_H values) for temperatures close to 25°;^{2b} and (d) utilization of the calorimetrically obtained data of Hepler, *et al.*,⁴ for reactions of type 2. The combination of data for reactions 3 and

2 then provided the required information for the various reactions 1.

In these previous studies of reaction 3 we have in general used solutions which were $\sim 10^{-3} M$ in iron(III). The method used to evaluate the various k_x requires that Fe^{3+} , FeOH^{2+} , and $\text{FeOC}_6\text{H}_4\text{X}^{2+}$ are the only species of iron(III) present at significant concentrations. The $\text{Fe}_2(\text{OH})_2^{4+}$ ion becomes increasingly important as the acidity of solutions becomes lower,⁵ and data had therefore not been included where calculation indicated that 3% or more of the iron(III) would be in this dimeric form. The procedure nevertheless left moderately large uncertainties in the absolute values of k_x , largely because of necessarily lengthy extrapolations in the $1/A$ vs. $[\text{H}^+]$ plots and the possible influences on intercepts caused by the still remaining iron(III) (<3%) in the form of $\text{Fe}_2(\text{OH})_2^{4+}$. In the present study uncertainties arising from the above source have been markedly reduced by making measurements with $2 \times 10^{-4} M$ iron(III) solutions with use of 10-cm spectrophotometric cells. In this way the importance of $\text{Fe}_2(\text{OH})_2^{4+}$ and the possible importance of other polymeric species has been reduced to a level which we consider to be negligible, and the need for lengthy extrapolations in the $1/A$ vs. $[\text{H}^+]$ plots has been minimized. Also, because of the decreased iron(III) concentration, it has been possible to calculate equilibrium hydrogen ion concentrations, $[\text{H}^+]$, from stoichiometric hydrogen ion concentrations with increased and now extreme precision. We have further modified the earlier procedure in which Hepler's ΔH values for reaction 2 at zero ionic strength were used in conjunction with our data for ionic strength 0.10.⁶ The need for this procedure has been eliminated by measuring all required ΔG and ΔH values for reactions 2 at ionic strength 0.10 with use of the method of Robinson, *et al.*⁷

(1) Supported by Research Grants GM-07493 from the National Institute of General Medical Sciences, Public Health Service, and GP-6383 from the National Science Foundation.

(2) (a) R. M. Milburn, *J. Am. Chem. Soc.*, **77**, 2064 (1955); (b) K. E. Jabalpurwala and R. M. Milburn, *ibid.*, **88**, 3224 (1966).

(3) R. M. Milburn, *ibid.*, **89**, 54 (1967).

(4) (a) L. P. Fernandez and L. G. Hepler, *ibid.*, **81**, 1783 (1959); (b) L. G. Hepler, *ibid.*, **85**, 3089 (1963); (c) H. C. Ko, W. F. O'Hara, T. Hu, and L. G. Hepler, *ibid.*, **86**, 1003 (1964).

(5) (a) R. M. Milburn and W. C. Vosburgh, *ibid.*, **77**, 1352 (1955); (b) R. M. Milburn, *ibid.*, **79**, 537 (1957).

(6) The assumption made here was that changes in ΔH with ionic strength for reaction 2 would be small or at least essentially constant for the various phenols.

(7) (a) R. A. Robinson and A. I. Biggs, *Trans. Faraday Soc.*, **51**, 901 (1955); (b) G. F. Allen, R. A. Robinson, and V. E. Bower, *J. Phys. Chem.*, **66**, 171 (1962).

Experimental Section

Materials. Phenol and the chlorophenols were purified by distillation in nitrogen under reduced pressure. *p*-Nitrophenol and *m*-nitrophenol were recrystallized from chloroform (mp 113 and 96°, respectively). The *p*-formylphenol, purified by repeated recrystallization from water, was dried *in vacuo* over phosphorus pentoxide (mp 115°). The cyanophenols (Aldrich Chemical Co.) were recrystallized from carbon tetrachloride (mp 93, 78, and 111°, respectively, for the *ortho*, *meta*, and *para* derivatives). All melting points are in good agreement with literature values.

Iron(III) perchlorate (G. F. Smith, violet) was recrystallized from aqueous perchloric acid. Solutions of iron(III) perchlorate, perchloric acid, and sodium perchlorate were prepared and analyzed as previously described.^{2,3} All studies utilized aqueous NaClO₄-HClO₄ media with a total ionic strength of 0.10 *M*. For the iron(III) phenolysis studies the iron(III) concentration was $\sim 2 \times 10^{-4}$ *M*, while the total phenol concentrations were varied from 0.04 to 0.15 *M* depending upon the solubilities of phenols and absorbancy coefficients of the complexes.

Buffer solutions required for ionization studies of phenols were prepared by mixing 50 ml of 0.2 *M* tris(hydroxymethyl)amino-methane (THAM) in 0.200 *M* NaClO₄, *x* ml of 0.200 *M* HCl, and (50 - *x*) ml of 0.200 *M* NaClO₄. The buffer solution of desired pH was obtained by varying *x*. These buffer solutions, after mixing with equal volumes of phenol solution (concentrations $\sim 10^{-4}$ to 10^{-5} *M*) gave the ionic strength 0.10 *M*. It should be noted that hydrochloric acid was not used in any studies involving iron(III) solutions.

Technique, Calculations, and Results

A. Iron(III) Phenolysis (Reactions 3). Apart from the modifications which have been described, the procedures used to study reactions 3 were similar to those outlined in the preceding paper.³ Absorbance measurements on iron(III)-phenol solutions with hydrogen ion concentrations in the range ~ 4 - 15×10^{-3} *M* were carried out with a Cary 14 spectrophotometer, using 10-cm cells with a jacket through which thermostated water was circulated. Temperatures in the cells were measured to within $\pm 0.1^\circ$ with a calibrated thermistor apparatus. In the case of unsubstituted phenol and *o*-chlorophenol, where slow redox reactions occur, the absorbance was noted at various times and extrapolated to zero time. In these cases component iron(III) and phenol solutions were brought to reaction temperature with the iron(III) solution in the cell, and at zero time the phenol was added by means of a syringe. The absorbance could then be recorded from the first minute after mixing. For the reaction conditions used, the only iron(III)-phenolate species of importance are the 1:1 complexes (FeOC₆-H₄X²⁺) as indicated by evidence previously cited.^{2a} This evidence includes carefully controlled continuous variations and transport experiments, strict linearity in plots of $1/A$ vs. $[H^+]$, and independence in values of k_x (equilibrium quotients for reactions 3) on the phenol concentration.

The k_x values were measured at known temperatures close to 25°, and also, in accord with the previously described method,³ at known temperatures close to 15 and 35°. Values of k_x corrected to 25.0°, obtained from least-squares plots of $\log k_x$ vs. $1/T(^{\circ}K)$, are: H, 0.92×10^{-2} ; *p*-NO₂, 1.39×10^{-2} ; *m*-NO₂, 0.94×10^{-2} ; *p*-CN, 1.26×10^{-2} ; *m*-CN, 0.91×10^{-2} ; *o*-CN, 4.84×10^{-2} ; *p*-Cl, 0.60×10^{-2} ; *m*-Cl, 1.26×10^{-2} ; *o*-Cl, 0.69×10^{-2} ; *p*-CHO, 0.92×10^{-2} . The value for phenol itself is essentially the same as found in the preceding study,³ while the values for the other three phenols included in the preceding study are slightly lower

Table I. Thermodynamic Data for Phenolysis Reactions of Type 3, at 25.0° and Ionic Strength 0.10

X	ΔG , kcal mole ⁻¹	ΔH , kcal mole ⁻¹	$-T\Delta S$, kcal mole ⁻¹	ΔS , eu
H	+2.8	+5.6	-2.8	+9
<i>p</i> -NO ₂	+2.5	+5.3	-2.8	+9
<i>m</i> -NO ₂	+2.7 ₅	+5.8	-3.0 ₅	+10
<i>p</i> -CN	+2.6	+4.6	-2.0	+7
<i>m</i> -CN	+2.8	+6.2	-3.4	+11
<i>o</i> -CN	+1.8	+4.7	-2.9	+9
<i>p</i> -Cl	+3.0	+4.9	-1.9	+6
<i>m</i> -Cl	+2.6	+5.9	-3.3	+11
<i>o</i> -Cl	+2.9 ₅	+4.9 ₅	-2.0	+7
<i>p</i> -CHO	+2.8	+4.5	-1.7	+6

Table II. Thermodynamic Data for Proton-Phenolate Association Reactions of Type 2, at 25.0° and Ionic Strength 0.10

X	ΔG , kcal mole ⁻¹	ΔH , kcal mole ⁻¹	$-T\Delta S$, kcal mole ⁻¹	ΔS , eu
H	-13.4	-6.1	-7.3	+24
<i>p</i> -NO ₂	-9.4	-4.8	-4.6	+15
<i>m</i> -NO ₂	-11.1	-4.8	-6.3	+21
<i>p</i> -CN	-10.5	-4.8	-5.7	+19
<i>m</i> -CN	-11.4	-5.3	-6.1	+20
<i>o</i> -CN	-9.3 ₅	-4.0	-5.3 ₅	+18
<i>p</i> -Cl	-12.5	-6.1	-6.4	+21
<i>m</i> -Cl	-12.0	-6.1	-5.9	+19
<i>o</i> -Cl	-11.2 ₅	-4.7 ₅	-6.5	+22
<i>p</i> -CHO	-10.1	-4.0	-6.1	+20

Table III. Thermodynamic Data for Iron(III)-Phenolate Association Reactions of Type 1, at 25.0° and Ionic Strength 0.10

X	ΔG , kcal mole ⁻¹	ΔH , kcal mole ⁻¹	$-T\Delta S$, kcal mole ⁻¹	ΔS , eu
H	-10.6	-0.5	-10.1	+33
<i>p</i> -NO ₂	-6.9	+0.5	-7.4	+24
<i>m</i> -NO ₂	-8.3	+1.0	-9.3	+31
<i>p</i> -CN	-7.9	-0.2	-7.7	+26
<i>m</i> -CN	-8.6	+0.9	-9.5	+31
<i>o</i> -CN	-7.5 ₅	+0.6 ₅	-8.2	+27
<i>p</i> -Cl	-9.5	-1.2	-8.3	+28
<i>m</i> -Cl	-9.4	-0.2	-9.2	+31
<i>o</i> -Cl	-8.3	+0.2	-8.5	+28
<i>p</i> -CHO	-7.3	+0.5	-7.8	+26

than before. The influence of Fe₂(OH)₂⁴⁺ in the more concentrated (10^{-3} *M*) iron(III) solutions, which would be of greatest importance for solutions of lowest acidity, would be in a direction to make the measured k_x appear larger than the true values.

The thermodynamic data for reactions of type 3 are summarized in Table I. Uncertainties in the ΔG , ΔH , and $-T\Delta S$ values are of the order ± 0.15 , ± 0.25 , and ± 0.4 kcal mole⁻¹, respectively.

B. Ionization of Phenols. The ionization equilibrium quotient ("concentration" equilibrium constant) for a monobasic phenol, *K*, is related to the fraction α of phenol ionized by

$$pK = p[H^+] - \log\left(\frac{\alpha}{1-\alpha}\right)$$

For the establishment of the various *K* at ionic strength 0.10, α values were obtained spectrally from $(A - A_1)/$

($A_2 - A_1$) where A_1 , A_2 , and A are, respectively, the absorbance in acid, alkaline, and buffer solutions containing the same stoichiometric concentrations of phenol. A_1 and A_2 values were observed using 0.10 M $HClO_4$ and 0.10 M $NaOH$ media, respectively. The $p[H^+]$ values for the buffer solutions were obtained, as before,^{2b} from

$$pH_{measd} = p[H^+] - \log f$$

with the activity coefficient term calculated by the Davies equation⁸

$$-\log f = A \left\{ \frac{\mu^{1/2}}{1 + \mu^{1/2}} - 0.3\mu \right\}$$

For each phenol, measurements were made at temperatures of approximately 15, 20, 25, 30, and 35°, each known to $\pm 0.1^\circ$. The values of pH_{measd} for the buffer solutions were determined with a Radiometer pH meter. The spectral measurements, made with use of 1-cm thermostated cells, were carried out at six wavelengths near the absorbance maxima for basic solutions, the mean of the pK values being taken. Also, for each phenol two buffers having different pH_{measd} were used; these gave concordance of pK values to within ± 0.02 .

For each of the phenols, plots of pK vs. $1/T(^{\circ}K)$ were obtained. From the least-squares lines the pK values for 25.0° are: H, 9.80; $p-NO_2$, 6.89; $m-NO_2$, 8.12; $p-CN$, 7.71; $m-CN$, 8.34; $o-CN$, 6.86; $p-Cl$, 9.16; $m-Cl$, 8.80; $o-Cl$, 8.25; $p-CHO$, 7.38. These pK values, after correcting for activity coefficients, are in generally good agreement with previous reliable values in the literature.⁹ The constants for 25° are linearly related to the Hammett σ values⁹ by

$$pK = 9.75 - 2.28\sigma$$

such that the mean difference between observed and calculated pK values is 0.03. This result is in good accord with the relationship given by Biggs and Robinson.¹⁰

In Table II we summarize our thermodynamic data for the proton-phenolate association reactions of type 2 at 25°. Uncertainties in the ΔG , ΔH , and $-T\Delta S$ values are of the order ± 0.1 , ± 0.2 , and ± 0.3 kcal mole⁻¹, respectively. The values agree fairly well with data obtained previously for certain of the phenols.^{4,7,10,11}

Table III summarizes the data for reactions of type 1 as calculated from Tables I and II. Uncertainties in the ΔG , ΔH , and $-T\Delta S$ values are of the order ± 0.2 , ± 0.4 , and ± 0.6 kcal mole⁻¹, respectively.

Discussion

As described above, the data obtained in the present study can be considered to be quantitatively more reliable than that included in the preceding report.³ For those phenols common to both studies, however, the quantitative differences are in general not large, and the qualitative conclusions drawn in our earlier report remain unchanged.

Among the more significant of the conclusions arising

(8) C. W. Davies, "Ion Association," Butterworth, Inc., Washington, D. C., 1962, p 41.

(9) G. B. Barlin and D. D. Perrin, *Quart. Rev.* (London), **20**, 75 (1966).

(10) A. I. Biggs and R. A. Robinson, *J. Chem. Soc.*, 388 (1961).

(11) R. A. Robinson and A. Peiperl, *J. Phys. Chem.*, **67**, 2860 (1963).

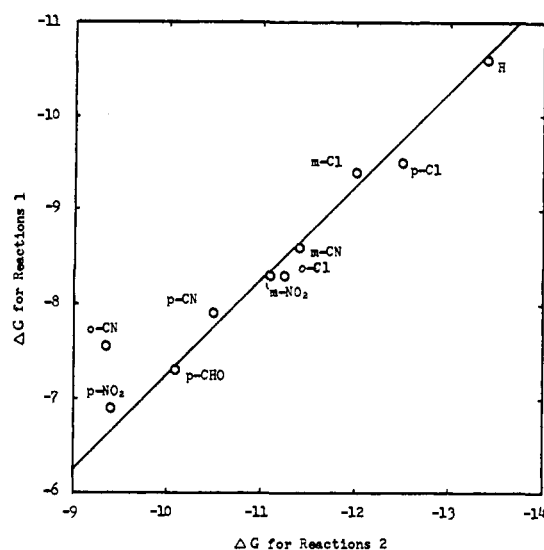


Figure 1. Comparison of ΔG values for reactions of types 1 and 2. Values are in kilocalories per mole; line is of unit slope.

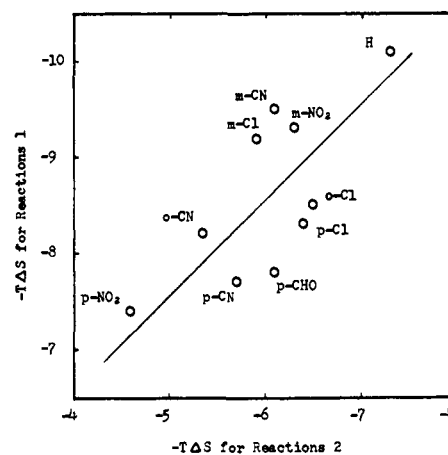


Figure 2. Comparison of $-T\Delta S$ values for reactions of types 1 and 2. Values are in kilocalories per mole; line is of unit slope.

from this and the preceding study concerns the importance of entropy effects in relation to iron(III)-phenolate complex formation. Thus, while the enthalpy changes for reactions 3 are all unfavorable, reaction entropies all favor complex formation. For reactions of type 1, the entropy changes are clearly dominant in determining the reaction feasibilities. In regard to the influence of individual substituents, the situation for reactions of type 1 in general closely parallels that prevailing for the corresponding proton-phenolate associations (reactions 2). Thus, in comparing *m*- and *p*-nitrophenolate ions, the more favorable free-energy changes for association of the *meta* isomer with both iron(III) ion and hydrogen ion are due to the more favorable entropy changes. These more favorable reaction entropies for *m*-nitrophenolate are attributed to a greater degree of solvent release accompanying reaction, the anion of the *meta* isomer presumably being more heavily hydrated because of a greater degree of charge localization.^{3,4} Several analogous situations are observed among the additional

phenols which have now been examined in detail. For example, the greater affinity of *m*-cyanophenolate ion for iron(III) ion compared to *p*-cyanophenolate is again attributable to the more favorable reaction entropy. More generally, it may be seen from Table III that the most positive entropies of reaction are found for unsubstituted phenol and its *meta*-substituted derivatives.

In Figure 1 is shown a plot between the ΔG values for reactions of types 1 and 2. With the exception of *o*-CN, the points correspond closely to the previously observed straight line of unit slope.^{2,3} The point for *o*-Cl falls close to the line correlating the *meta* and *para* substituents, similar to the situation observed before^{2b,12} for this and other *o*-halo substituents and for *o*-NO₂. The absence of significant scatter for this group of *ortho* substituents suggests that any special interactions between iron(III) ion and the substituents are closely matched by proton-substituent interactions in the free phenol. For *o*-CN, however, the iron(III) complex exhibits an abnormal stability corresponding to a free-energy difference of nearly 1 kcal mole⁻¹.

In accord with earlier discussion,^{2b,3} the free-energy correlation of the type shown in Figure 1, together with the well-established relation between ΔG values for reactions 2 and Hammett's σ substituent constants, strongly suggests that $\delta\Delta G$ values for reactions 1, like reactions 2, are a fair measure of relative changes in bond energies within the solute species. Such "internal" contributions to the stabilities may be rationalized in terms of inductive and resonance effects. There is, however, no obvious correlation between the ΔH and ΔG values for either reactions 1 or 2, as illustrated by a comparison of *m*- and *p*-nitrophenol, or, more generally, by a plot of ΔH

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

against ΔG for either of the reaction series. The simple linear free-energy relation of Figure 1 clearly arises because of an approximate cancellation of the $\delta\Delta H_{\text{ext}}$ values with $-T\delta\Delta S$ values for the reactions. Thus, for each of reactions 1 and 2 one can write^{3,4}

$$\delta\Delta G = \delta\Delta H_{\text{int}} + \delta\Delta H_{\text{ext}} - T(\delta\Delta S_{\text{int}} + \delta\Delta S_{\text{ext}})$$

But, as has been argued, for these reactions $\delta\Delta S_{\text{int}} \sim 0$ and $\delta\Delta H_{\text{ext}} \sim \beta\delta\Delta S_{\text{ext}}$, with β in the vicinity of 280° (*i.e.*, each reaction type has an isoequilibrium temperature for the "external" interaction mechanism in the vicinity of room temperature). Hence, for each of reactions 1 and 2, $\delta\Delta G \sim \delta\Delta H_{\text{int}}$. The linear unit-slope ΔG vs. ΔG relation then arises because the substituents have quantitatively similar effects on the internal bonding for reactions 1 and 2. This fact argues for the predominant importance of σ bonding and suggests that π bonding in these iron(III) complexes is unimportant. This is contrary to some views which have been expressed by others.¹²⁻¹⁴

In the preceding study,³ which involved just four phenols, it was noted that the entropy changes for reactions 1 and 2 were correlated moderately well by a straight line of unit slope. The relationship between entropy changes measured in the present study for the two reaction series is shown in Figure 2. While significant scatter is observed, the distribution of points within probable limits of error for individual values can still be described by a unit-slope straight line. This is consistent with the existence of a similar pattern of solvation effects for the two reaction series.

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

(14) M. V. Park, *ibid.*, A, 816 (1966).