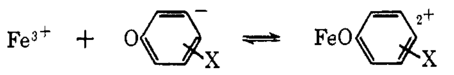
Iron(III)-Phenol Complexes. III. Enthalpies and Entropies of Iron(III)-Phenolate Associations[1,2]

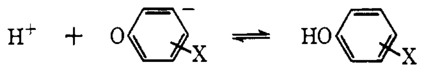
Ronald M. Milburn

Contribution from the Department of Chemistry, Boston University, Boston, Massachusetts. Received July 22, 1966

Abstract: Enthalpy changes in aqueous solution for reactions of type $Fe^{3+} + HOC_6H_4X \rightleftarrows FeOC_6H_4X^{2+} + H^+$ have been measured by a spectrophotometric method based on the conclusion that the absorptivity coefficients of the iron(III)-phenolate complexes are, in the vicinity of the visible band maxima, insensitive to small changes in temperature. With X equal to H, *p*-Cl, *p*-NO_2, and *m*-NO_2 respective values of ΔH for 25° and ionic strength 0.10 are +5.6, +5.6, +5.0, and +5.9 kcal/mole, with uncertainties of ±0.3 kcal. These values, together with our spectrophotometrically obtained free-energy data for 25° and the calorimetric data of Hepler for corresponding phenolic acid dissociations, have been used to calculate enthalpy and entropy changes for the association reactions of type $Fe^{3+} + OC_6H_4X^- \rightleftarrows FeOC_6H_4X^{2+}$. At 25° and ionic strength 0.10, with X equal to H, *p*-Cl, *p*-NO_2, and *m*-NO_2, the respective ΔH values are −0.1, −0.2, +0.3, and +1.2 kcal/mole, while corresponding values of $T\Delta S$ are 10.6, 9.6, 7.5, and 9.7. Uncertainties in the relative values of ΔH and $T\Delta S$ are of the order ±0.3 and ±0.4 kcal, respectively. The results demonstrate the extreme importance of entropy factors in determining both the individual and the relative stabilities of the various iron (III)-phenolate complexes. A thermodynamic assessment of possible bonding differences between corresponding metal-ligand and proton-ligand complexes suggests that π bonding in the iron(III) complexes is unimportant. The free-energy values for the formation of iron(III)-phenolates would appear to give a fair measure of the relative changes in internal bond energy accompanying complex formation.

Recently we have described[3] the measurement of equilibrium quotients for reactions of types 1 and 2 for a series of closely related *ortho*, *meta*, and *para* singly substituted phenols. These results, as with those of earlier studies,[4,5] point to a moderately good linear relation between the free-energy changes for reactions of types 1 and 2.


(1)


(2)

In any attempt to analyze in detail the quantitative effect of substituents it is important to be able to divide the reaction free-energy changes into the enthalpy and entropy contributions. Enthalpy changes for reactions of type 2 are available in certain cases, particularly through the calorimetric studies of Hepler, *et al.*[6] On the other hand, accurate calorimetric determination of enthalpy changes associated with the formation of the 1:1 iron(III)-phenolate complexes would be difficult. Thus, the concentrations of iron(III) and phenol must be kept low to avoid polynuclear species and higher complexes,[4,7] and the competing hydrolysis of the iron(III) must be taken into account. The concentrations of iron(III)-phenolate complex will in all cases be small, and this will be reflected in small measured heat changes. A further limitation on a calorimetric determination is imposed by the precision of the formation equilibrium quotients, which in the present case, as explained below, is not high. We have, however, devised a simple spectrophotometric technique which allows measurement of the enthalpies for reactions of type 3 with good precision, and the method has been utilized for the substituents H, *p*-Cl, *p*-NO_2, and *m*-NO_2. The results, together with Hepler's data, allow a comparison of the enthalpy and entropy changes for reactions of types 1 and 2. The resulting data emphasizes the dominant importance of entropy considerations.


(3)

Experimental Section

Reaction Conditions and Materials. All studies utilized $NaClO_4$-$HClO_4$ media with total iron(III) concentrations equal to 10^{-3} *M* and total ionic strength equal to 0.10 *M*. The total phenol concentration was 0.040 *M* for *m*-nitrophenol and 0.050 *M* for the three other phenols. Solutions of iron(III) perchlorate, phenols, perchloric acid, and sodium perchlorate were prepared as previously described.[3,4]

Technique and Results. For the examination of each phenol, series of solutions covering the acid range ~4–18 × 10^{-3} were prepared from a solution containing the phenol and solutions containing iron(III) perchlorate together with appropriate amounts of $HClO_4$ and $NaClO_4$. The component phenol and iron(III) solutions were brought to reaction temperature, mixed, and quickly transferred to a thermostated 1-cm cell in a Beckman DU spectrophotometer. The absorbance was measured in the vicinity of the visible band maxima about 1 min after mixing, and the difference between the temperature of the cell and that of a bath of similar and known temperature was immediately measured with a calibrated thermistor temperature-difference device. In most cases additional measurements of the absorbances and cell temperatures were made over periods ranging from 5 to 30 min. Chemical

---

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

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

[3] K. E. Jabalpurwala and R. M. Milburn, *J. Am. Chem. Soc.*, **88**, 3224 (1966).

[4] R. M. Milburn, *ibid.*, **77**, 2064 (1955).

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

[6] (a) L. P. Fernandez and L. G. Hepler, *J. Am. Chem. Soc.*, **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).

[7] Most of the phenols under study have, in any event, only low solubilities in water.

equilibrium in the iron(III)–phenolate systems is achieved very rapidly, and, except in the case of the unsubstituted phenol where slower redox reactions occur, the absorbances were independent of time for a given solution temperature. For each iron(III)–phenol system the absorbance measurements were made at temperatures close to 15, 25, and 35°.[8] The procedure enabled absorbances of equilibrated solutions to be measured at temperatures known to ±0.1°.

Reaction conditions were chosen, as for earlier work,[3,4] so that Fe^{3+}, $FeOH^{2+}$, and $FeOC_6H_4X^{2+}$ would be the only iron(III) species present at significant concentrations.[9] When spectral measurements are then in a region where $FeOC_6H_4X^{2+}$ alone absorbs, we have[4]

$$1/A = (1/C_{Fe}e_x)\left\{1 + \frac{k_1}{[HOC_6H_4X]k_x} + \frac{[H^+]}{[HOC_6H_4X]k_x}\right\} \quad (4)$$

where brackets refer to equilibrium concentrations, A is the absorbance of solutions for a 1-cm cell, e_x is the absorbancy coefficient for $FeOC_6H_4X^{2+}$, C_{Fe} is the stoichiometric concentration of iron(III), k_x is the equilibrium quotient for the phenolysis reaction as expressed by eq 3, and k_1 is the equilibrium quotient for the first hydrolysis reaction

$$Fe^{3+} + H_2O \rightleftharpoons FeOH^{2+} + H^+ \quad (5)$$

Because the stoichiometric concentrations of phenol are taken in large excess to C_{Fe}, they may be identified with the equilibrium concentrations $[HOC_6H_4X]$. Hence, for a given temperature and ionic strength eq 4 predicts a linear relation between $1/A$ and $[H^+]$ which will allow the evaluation of k_x and e_x from

$$k_x = \{(\text{intercept/slope}) - k_1\}/[HOC_6H_4X] \quad (6)$$

$$e_x = 1/C_{Fe}\{\text{intercept} - k_1(\text{slope})\} \quad (7)$$

Values of k_1 are available at various ionic strengths and temperatures from previous work.[10,11]

For each of the four phenols, plots of $1/A$ *vs.* $[H^+]$ were obtained for three temperatures. Values of $[H^+]$ were obtained from the stoichiometric acid concentration together with minor correction for the small amounts of acid produced by hydrolysis and phenolysis. These corrections were obtained, as has been described,[4] using the appropriate values of k_1 and values of k_x which were improved by a reiterative process.[12]

In Figure 1 we show plots of $1/A$ *vs.* $[H^+]$ (corrected as described) for the iron(III)–*p*-nitrophenol system at three temperatures. Good linearity is obtained at each temperature, so that it is possible to calculate values of k_x and e_x from eq 6 and 7. Similarly for the other phenols one obtains linear plots between $1/A$ and $[H^+]$ for each temperature.

With reference to eq 6 we see that a difference is involved in the evaluation of k_x, and because the intercept is not defined with good precision due to the necessary extrapolation, it cannot be argued that the individual values of k_x will be particularly precise. Therefore, one can hardly hope to obtain reliable values of ΔH from k_x values obtained independently using eq 6 at each of several temperatures.

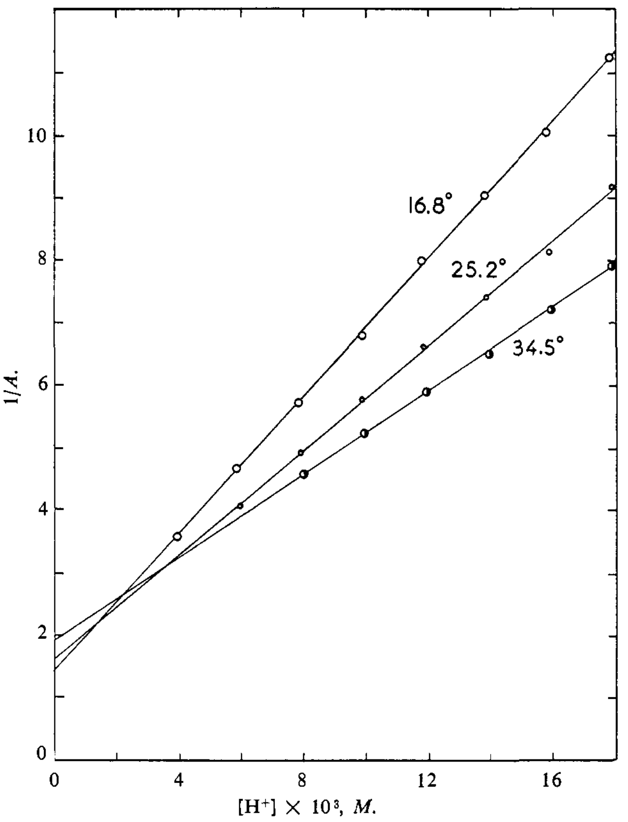


Figure 1. Plots of $1/A$ against $[H^+]$ for the *p*-nitrophenol–iron(III) system. Ionic strength 0.10; wavelength 550 mμ.

The problem is capable of resolution, however, in the case where the absorbancy coefficients of the $FeOC_6H_4X^{2+}$ ions are insensitive to small changes in temperature. One cannot directly determine any temperature dependence of the coefficients satisfactorily, since the e_x values measured by means of eq 7 are also relatively imprecise, depending on a difference between the intercept (imprecisely defined) and a product of two independent experimentally determined quantities.[13] These visible spectra are, however, commonly interpreted as being of charge-transfer type corresponding to allowed transitions.[14–17] In accord with this view the absorbancy coefficients of the complexes under examination are, at the maxima, in excess of 10^3 as previously observed.[4] For such a case, in the vicinity of the observed broad maxima, one would expect very little change in the absorbancy coefficients over temperature ranges as small as those involved in the present study. In support of this view we have examined the charge-transfer bands for several *nonlabile* complexes ($[Ru(NH_3)_5Cl]Cl_2$; $[Ru(NH_3)_5Br]Br_2$; $[Co(NH_3)_5Cl]Cl_2$) over a comparable 20° range in temperature, and find that between the band maxima and the half-height the absorbancy coefficients change by not more than about 1%. In addition, it may be noted that for the analogous reaction

$$Fe^{3+} + Cl^- \rightleftharpoons FeCl^{2+}$$

the measured ΔH, as obtained from spectral data corresponding to an absorption maximum for the $FeCl^{2+}$ ion, agrees well with the values obtained both from emf and from calorimetric measure-

---

(8) Because at ~15° *p*-nitrophenol tends to deposit from 0.1 *M* solution, the final iron(III)–phenol solutions were in this case prepared by mixing component solutions at room temperature and rapidly cooling to the required temperature.

(9) Data were discarded in cases where calculation indicated that 3% or more of the iron(III) would be in the form $Fe(OH)_2Fe^{4+}$. This species does not absorb in the spectral range of interest.

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

(11) R. M. Milburn, *ibid.*, 79, 537 (1957).

(12) For the measurements at ~25° a plot of $1/A$ *vs.* $[H^+]$, corrected for hydrolysis only, allows a first estimate of k_x. This estimate together with k_1 then provides improved estimates of $[H^+]$, and hence by a further $1/A$ *vs.* $[H^+]$ plot a second and improved estimate of k_x. In practice values of k_x and $[H^+]$ become constant after two reiterations of the process. For the measurements at ~15 and ~35° the estimates of k_x were obtained using eq 9, which is described below.

(13) Within the rather broad limits of experimental error the measured values of e_x show no apparent trend with temperature.

(14) N. S. Hush, *Rec. Trav. Chim.*, 75, 1101 (1956).

(15) J. C. Tomkinson and R. J. P. Williams, *J. Chem. Soc.*, 1153 (1958).

(16) L. E. Orgel, "An Introduction to Transition Metal Chemistry. Ligand Field Theory," John Wiley and Sons, Inc., New York, N. Y., 1960, p 101.

(17) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press Inc., New York, N. Y., 1962, p 195.

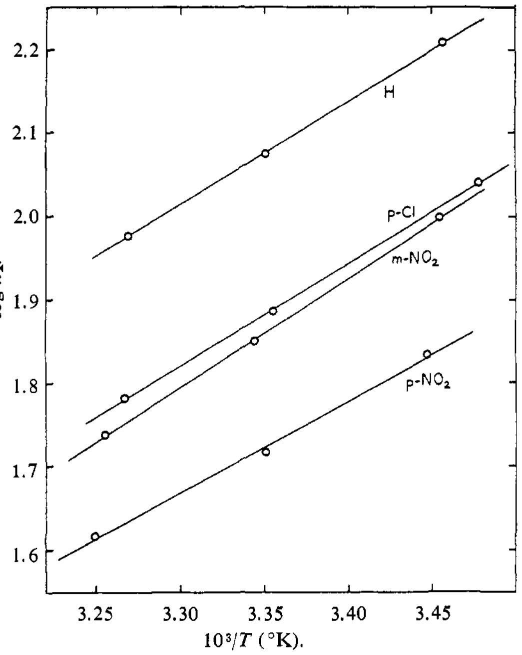


Figure 2. Determination of ΔH for reactions 3 from plots of log k_x against $1/T$(°K).

ments.[18] Again our earlier assumption that absorptivity coefficients of the $FeOH^{2+}$ ion will be independent of temperature[11] has been given support by the work of Richards and Sykes.[19] It thus seems reasonable to conclude that the absorptivity coefficients of the $FeOC_6H_4X^{2+}$ ions will be, in the vicinity of the band maxima, essentially independent of temperature over the range of our experiments.

Now, from eq 6 and 7, we can write

$$k_x = \frac{1}{e_x C_{Fe}(\text{slope})[HOC_6H_4X]} \qquad (8)$$

and where e_x is independent of temperature

$$\frac{k_x'}{k_x''} = \frac{\text{slope}''}{\text{slope}'} \qquad (9)$$

where the single and double primes refer to two temperatures. The slopes of the $1/A$ *vs.* $[H^+]$ plots are precisely defined, and by use of eq 9 the temperature dependence of k_x may now be determined with a respectable degree of precision. It may be noted that a determination of k_x'/k_x'' does not depend on knowledge of the hydrolysis constant k_1, or its temperature dependence, nor does it require knowledge of e_x.

In Figure 2 are shown plots of log k_x *vs.* $1/T$(°K). The k_x values in the vicinity of 25° were obtained using eq 6, with the least-squares intercepts and slopes, while the k_x values for ~15 and ~35° were obtained using eq 9 with the least-squares slopes for ~25° and the appropriate other temperature. Values of k_x for 25.0°, taken from the values for ~25° with correction for the small temperature differences, are: H, 0.83×10^{-2}; *p*-Cl, 1.31×10^{-2}; *p*-NO$_2$, 1.91×10^{-2}; *m*-NO$_2$, 1.39×10^{-2}.

Table IA summarizes the thermodynamic data for reactions of type 3 as obtained herein. It may be noted that the values of ΔH, which were obtained from the least-squares slopes of the lines in Figure 2, are *independent* of the absolute values of k_x.

Table IB includes our earlier free-energy data[3] for the proton association reactions of type 2 at 25° and ionic strength 0.10, and the calorimetrically determined ΔH values of Hepler, *et al.*[6] Although the latter data refer to zero ionic strength, they have been used in conjunction with our data for the purposes of further calculation without adjustment for differences in ionic strength. Any errors introduced by the assumption that ΔH will be independent of ionic strength are likely to be small,[20] and, in any event, to be essentially constant for the various phenols. The tabulated entropy terms have been obtained directly from the appropriate ΔF and ΔH values.

Table IC summarizes the thermodynamic data appropriate for reactions of type 1 as calculated from the data in Tables IA and IB.

Table I

X	ΔF, kcal	ΔH, kcal	$-T\Delta S$, kcal	ΔS, eu
A. Data at 25.0° and Ionic Strength 0.10 for Reactions of Type 3				
H	+2.8	+5.6	−2.8	+9
p-Cl	+2.6	+5.6	−3.0	+10
p-NO$_2$	+2.3	+5.0	−2.6	+9
m-NO$_2$	+2.5	+5.9	−3.4	+11
B. Data at 25.0° for Reactions of Type 2[a]				
H	−13.5	−5.7	−7.8	+26
p-Cl	−12.4	−5.8	−6.6	+22
p-NO$_2$	−9.6	−4.7	−4.9	+16
m-NO$_2$	−11.0	−4.7	−6.3	+21
C. Data at 25.0° for Reactions of Type 1[b]				
H	−10.7	−0.1	−10.6	+36
p-Cl	−9.9	−0.2	−9.6	+32
p-NO$_2$	−7.2	+0.3	−7.5	+25
m-NO$_2$	−8.4	+1.2	−9.7	+33

[a] Values of ΔF refer to ionic strength 0.10; values of ΔH are those of Hepler, *et al.*[6] (see text). [b] Values have been computed directly from the data in A and B above (see text).

The data in Table I have been rounded off to the nearest 0.1 kcal. Uncertainties in the ΔF values for reactions 2 are of the order ±0.15 kcal,[3] while uncertainties in the relative values of ΔF for reactions 3 and 1 are of the order of ±0.2 kcal. The absolute values of ΔF for reactions 3 and 1 are somewhat less certain, but for the present the relative values will suffice to demonstrate some major points of interest.[21,22]

In regard to ΔH, for reaction 2 the relative values are probably reliable to ±0.1 kcal per mole; for reactions 3 and 1 uncertainties in relative values are of the order of ±0.3 kcal.[23] In consequence, the relative entropy contributions to reactions 3, 2, and 1 can be considered accurate to within ±0.4, ±0.2, and ±0.4 kcal per mole, respectively, or to slightly better than ±2, ±1, and ±2 eu.

Discussion

For the various reactions 3, as revealed by the data in Table IA, the values for each of the free energy,

---

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

(19) D. H. Richards and K. W. Sykes, *J. Chem. Soc.*, 3626 (1960).

(20) See, for example, T. W. Newton and G. M. Arcand, *J. Am. Chem. Soc.*, 75, 2449 (1953).

(21) For H, *p*-Cl, and *p*-NO$_2$ as substituents the ΔF values for reactions 3 agree within 0.1 kcal with the earlier spectrophotometric values[4,5] when the latter are corrected to ionic strength 0.10 on the assumption that the ionic strength dependence will be the same as that for reaction 5.[10] For *m*-NO$_2$ the agreement is less satisfactory, but use of the earlier value[4] extrapolated to ionic strength 0.10 would in fact only work in the direction of strengthening the major arguments presented below.

(22) The uncertainty in the absolute values is in part due to the lengthy extrapolation in the $1/A$ *vs.* $[H^+]$ plots and possible influences on the intercepts caused by the presence of small amounts (in all cases <3%) of iron(III) in the form of the $Fe(OH)_2Fe^{4+}$ ion. As has been indicated,[3] further investigations 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, are likely to lead to more reliable estimates for the absolute magnitudes of the ΔF values. Studies of this type are currently in progress.

(23) For reactions 3 we again refer to relative values because of a small influence which the presence of $Fe(OH)_2Fe^{4+}$ could have on the measured ΔH (all recorded values are probably low by about 0.2 kcal). Rather than attempting to correct for this effect at the present time, we have deemed it desirable to undertake a thorough reexamination of these systems (see also ref 22).

enthalpy, and entropy contributions are fairly similar; thus the substituents X have no obviously marked effect on the way that iron(III) and the proton compete for the phenolate residue. The essentially constant entropy term, corresponding to about +10 eu, points to a similar degree of solvent release on complexing. In his study of chelating phenols Ågren similarly observed[24] constant entropies of reaction when the iron(III) ion displaces a phenolic proton; the larger entropies for these cases ($\sim$+28 eu in the 3 *M* ClO_4^- media) are at least in part related to a greater degree of solvent release on chelation. For the hydrolysis reaction 5 it may be noted that the entropy of reaction for ionic strength 0.1 will be about +23 eu,[11] suggesting that there is significantly greater solvent release associated with the process $H_2O(l) \rightarrow OH^-(\text{bound}) + H^+(l)$ than with the process $HOC_6H_4X(l) \rightarrow OC_6H_4\text{-}X^-(\text{bound}) + H^+(l)$.

It is especially revealing to compare reactions 2 (Table IB) with reactions 3 (Table IC).

For the proton–phenolate associations it is seen that the enthalpy and entropy terms make comparable contributions to the free-energy changes, both terms heavily favoring reaction. In the case of the iron(III)–phenolate associations the entropy contributions are clearly dominant; indeed, if it were not for the entropies the reactions either would not be or would scarcely be thermodynamically favorable.

In analyzing the influence of substituents on phenolic acid dissociations Hepler, *et al.*,[6] have emphasized the importance of entropy considerations. For example, the proton associates more readily with *m*-nitrophenolate than with *p*-nitrophenolate because of a more favorable entropy of reaction and not because the former reaction is more exothermic (the heats of reaction are the same).

In comparing the effect of substituents on the iron(III)–phenolate associations we likewise find entropy considerations to be of extreme importance. Thus iron(III) ion forms a stronger complex with *m*-nitrophenolate than with *p*-nitrophenolate, *not* because of the relative reaction enthalpies (which would in fact slightly favor the association with *p*-nitrophenolate) *but* because of the more favorable entropy of reaction. As with the proton associations, the more favorable entropy change in the case of the iron(III) association with *m*-nitrophenolate probably arises because of a greater degree of hydration of the latter ion compared to *p*-nitrophenolate (the negative charge for the *meta* isomer being more localized on the phenolic oxygen) and a consequent greater degree of solvent release on complexing. For other pairs of phenols similar comparisons can be made. Thus, in comparing iron(III) complexes of phenol and *p*-chlorophenol, or of *p*-chlorophenol and *p*-nitrophenol, entropy terms again dominate the scene.

The unit slope line between ΔF values for reactions 2 and 1, which was previously observed,[3,4] is reproduced fairly well, although displaced, when one examines the entropy contributions. The comparison is shown in Figure 3. The displacement is, of course, a measure of the differences in enthalpies for the two reaction series.

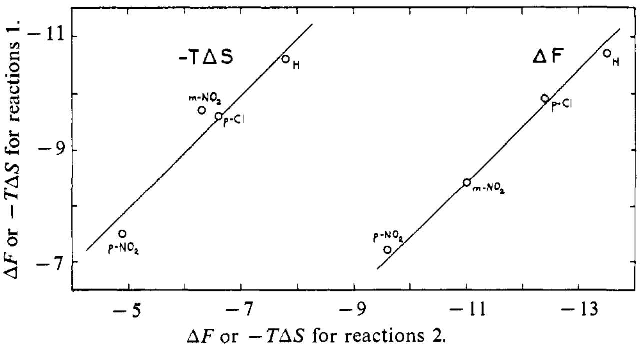


Figure 3. Comparison of ΔF and $-T\Delta S$ values for reactions of types 1 and 2. Values are in kilocalories per mole; lines are of unit slope.

Considerable use has been made of free-energy data in attempts to assess possible bonding differences between corresponding metal–ligand and proton–ligand complexes. Important limitations to this type of approach exist as we have previously emphasized with particular reference to the iron(III)–phenolate and proton–phenolate associations.[3] With the additional data at hand a slightly more detailed analysis is now possible.

Thus, for reactions in solution, and in particular for reactions of types 2 and 1, one can write[6b]

$$\Delta F = \Delta H_{\text{int}} + \Delta H_{\text{ext}} - T(\Delta S_{\text{int}} + \Delta S_{\text{ext}}) \qquad (10)$$

where the subscript int refers to contributions arising within the reactant species and the subscript ext to contributions from solute–solvent interactions. With respect to a ΔF *vs.* ΔF plot between reactions 2 and 1, to be able to equate deviations from linearity to differences which substituents X cause in the internal bond energies of iron(III) and proton complexes a linear relation should exist between the $(\Delta H_{\text{ext}} - T\Delta S)$ terms for the two series of reactions, and to be able to equate deviations from unity of slope to differences which substituents X cause in the internal bond energies of iron(III) and proton complexes a unit slope relation should exist between the $(\Delta H_{\text{ext}} - T\Delta S)$ terms for the two series of reactions. However, for reactions 2 one expects[6b]

$$\Delta H_{\text{ext}} = \beta\Delta S_{\text{ext}} + C = \beta\Delta S + C' \qquad (11)$$

where β, C, and C' are constants, and on similar grounds for reactions 1 we might expect a relation of type

$$\Delta H_{\text{ext}} = \beta'\Delta S + C''$$

Linearity between the ΔS values for reactions of types 2 and 1 thus becomes a condition that deviations from linearity in the ΔF *vs.* ΔF plot should be a measure of differences in the internal bond energies of the metal–ligand and proton–ligand complexes. A unit slope relation between the ΔS values for reactions of types 2 and 1, as is observed herein within experimental error, suggests both that β and β' will have similar values and that deviations from unity of slope in a ΔF *vs.* ΔF plot would be a reflection of differences in metal–ligand and proton–ligand bond type.

---

(24) A. Ågren, *Svensk Kem. Tidskr.*, **68**, 185 (1956).

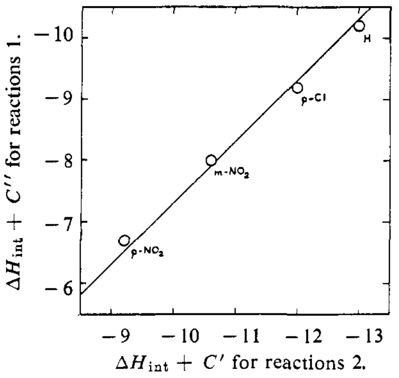


Figure 4. Comparison of relative values of ΔH_{int} for reactions of types 1 and 2, calculated on the premise that $\beta = \beta' = 280°$. Line is of unit slope.

The observation that there is in fact a rather good unit slope relation between the ΔF values for reactions of types 2 and 1, with little deviation of points,[3] coupled with the apparent unit slope relation between the entropies, argues for a lack of importance of π-bonding effects in the iron(III) complexes.

If, as indicated above, we accept the view that β' and β will be similar and adopt the value of 280° as utilized by Brown[25] and Hepler,[6] one can readily compute relative values of ΔH_{int} for reactions of type 1. These values and those for reactions of type 2 are compared in Figure 4. The observed linear relation is, of course, a close reflection of the ΔF *vs.* ΔF plot (Figure 3) since the choice $\beta = 280°$ results in essential cancellation of the ΔH_{ext} and $T\Delta S$ terms. This analysis, while only approximate, suggests that the ΔF values for reactions 1, as for reactions 2, will give a fair measure of the relative ΔH_{int} values. Within experimental limits the slope of the ΔH_{int} *vs.* ΔH_{int} plot is unity. It can scarcely be argued that the slope exceeds unity, as would be required[26] if the stabilities of the complexes were to be noticeably influenced by a capacity of the iron(III) to act as a π-electron acceptor.

Acknowledgment. Dr. K. E. Jabalpurwala, who made the major contribution to part II in this series,[3] conducted preliminary experimentation on the present aspect of the study and also kindly commented on the manuscript. His assistance is most gratefully acknowledged.

(25) (a) R. F. Brown, *J. Org. Chem.*, 27, 3015 (1962); (b) R. F. Brown and H. C. Newson, *ibid.*, 27, 3010 (1962).

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