ing that the rate of the forward reaction is the same in both equilibria. The variation in these reaction rates is related quantitatively to the relation between the constants K_S and K'_C (see equations 16 and 17), the charged amino group of the sulfonate ($K_S = 1.8 \times 10^{-9}$) being a stronger acid than that of reduced glutathione ($K'_C = 4.5 \times 10^{-10}$). The larger reaction rate between $\begin{array}{c}GS^-\\ |\\ NH_2\end{array}$ and $\begin{array}{c}GSSO_3^-\\ |\\ NH_3^+\end{array}$ may possibly be explained by assuming that the reaction between these two ions is initiated by an exchange of protons between the amino group of the sulfonate and that of reduced glutathione.

Comparing the three disulfides GSSG, RSSR and TSST it is seen that the constant K_I is largest for GSSG and smallest for TSST. Thus in alkaline medium the equilibrium involving TSST lies farthest to the left. Experiments to be reported in a subsequent paper on the alkaline fission of the three disulfides in the presence of silver or mercury salts indicate that cystine reacts the slowest and dithiodiglycolic acid the fastest. It thus appears that the reactivity of the three disulfide compounds toward sulfite is not related to their fissility in alkaline medium. It is interesting to note that in contrast to K_I, the values of K_V for the sulfite–disulfide system in acid medium are of the same order of magnitude for the three disulfides studied. This is accounted for by the numerical values of the constants which determine K_V (see equation 19 for GSSG and RSSR and equation 20[1] for TSST).

$$K_{V(TSST)} = \frac{K_{2(H_2SO_3)}K_I}{K_{(SH)}} \qquad (20)$$

where $K_{(SH)}$ is the dissociation constant of the sulfhydryl group of thioglycolic acid.

The numerical values of the ratios of the constant K_I and the dissociation constant of the sulfhydryl group (K_I/K'_4 for glutathione and cystine, $K_I/K_{(SH)}$ for dithiodiglycolic acid) are of the order of magnitude of 10^8 for the amino acids and 10^7 for TSST. The larger value (10^8) for GSSG and RSSR is multiplied by the term involving the dissociation constants of the NH_3^+ groups ($K'_5K'_6/K_SK'_3$ in equation 19) which is of the order of magnitude of 0.1, thus making the values of K_V of the three disulfides of the same order of magnitude. The numerical values of K_I and K_V of the three disulfides indicate that in alkaline medium equilibrium lies quite far to the left while in acid medium the equilibrium is more favored to the right side. The heat of reaction ΔH which has been determined only for glutathione and cystine is found to be of the same order of magnitude for the two acids.

TABLE II

EQUILIBRIUM CONSTANTS, CHANGE IN FREE ENERGY ΔF AND HEAT OF REACTIONS I, II, III, IV AND V FOR GLUTATHIONE (GSSG) AND CYSTINE (RSSR) AND OF REACTIONS I AND V FOR DITHIODIGLYCOLIC ACID (TSST)

	GSSG		RSSR		TSST
	12°	25°	12°	25°	25°
K_I	0.019	0.039	0.0060	0.010	0.00047
K_{II}	.0030	.0062	.00031	.00052	
K_{III}	.012	.025	.0095	.016	
K_{IV}	.018	.037	.086	.15	
K_V	1.3	2.6	2.5	4.1	1.4
ΔF_I, cal.	−2200	−1900	−2900	−2700	−4500
ΔF_{II} cal.	−3300	−3000	−4600	−4500	
ΔF_{III} cal.	−2500	−2200	−2600	−2500	
ΔF_{IV} cal.	−2300	−2000	−1400	−1100	
ΔF_V cal.	+140	+570	+290	+890	+200
ΔH, cal.	+9500		+7000		

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MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

N,N'-Dihydroxyethylglycine and its Complexes with Iron[1,2]

BY P. E. TOREN AND I. M. KOLTHOFF

RECEIVED OCTOBER 16, 1954

At an ionic strength of 0.5 the acid dissociation constants K_1 and K_2 of N,N'-dihydroxyethylglycine, (DHEG), are $10^{-2.50}$ and $10^{-8.11}$, respectively. Ferric and ferrous iron and their mixtures in the presence of excess DHEG give reversible waves at the dropping mercury electrode; the standard potential of the system is −0.94 v. *vs.* the saturated calomel electrode. The electrode reaction in neutral and alkaline solution is $FeG(OH)_2 + G^- + e \rightleftarrows FeG_2 + 2OH^-$. Potentiometric measurements at the platinum electrode indicate that the electrode reaction in acid solution is probably $FeG(OH)_2 + e \rightleftarrows Fe^{++} + G^- + 2OH^-$ between *p*H 5 and *p*H 3, and $Fe^{+3} + e \rightleftarrows Fe^{++}$ in more acid solutions. The complex stability constants determined from electrometric data are $K_{III} = 10^{30.1}$ and $K_{II} = 10^{5.9}$ for $FeG(OH)_2$ and FeG_2, respectively.

N,N'-Dihydroxyethylglycine (DHEG) is an amino acid with the structure R_2NCH_2COOH, where $R = C_2H_4OH$. In common with glycine and other amino acids, it is likely that the uncharged form of DHEG exists as a dipole ion, $R_2H^+NCH_2COO^-$. DHEG is a white solid which forms colorless aqueous solutions. Both the acid and its salt are soluble in water. In the present paper we report on the determination of the dissociation constants of DHEG and the stability constants of its ferric and ferrous complexes. Equations of the electrode reactions involving the ferric–ferrous complexes of DHEG at the dropping mercury and at a platinum electrode have also been established.

Materials.—The DHEG was furnished by the Alrose Chemical Company. It was purified by dissolving the acid in a small amount of hot water and precipitating with ethanol. A brown color which was not completely removed

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(1) This work was carried out under the sponsorship of the Reconstruction Finance Corporation, Office of Synthetic Rubber, in connection with the Synthetic Rubber Program of the United States Government.

(2) From a Ph.D. Thesis submitted by P. E. Toren to the Graduate School of the University of Minnesota, December, 1953.

after two crystallizations was eliminated by adding bone charcoal to the aqueous solution in the third crystallization, and filtering the solution before adding the alcohol. The final product was a fluffy pure white solid. Approximately 0.1 *M* solutions of DHEG were standardized by titration with sodium hydroxide using the glass electrode. The titration curves have an inflection point when equimolar amounts of DHEG and sodium hydroxide have reacted. The amount of base used corresponded to within 0.3% with the calculated amount. The amino group of the DHEG was titrated with perchloric acid in anhydrous acetic acid solution with crystal violet indicator.[3] The amino concentration corresponded to that calculated from the sample weight.

Stock solutions of ferric sulfate were prepared by dissolving Baker and Adamson Reagent grade $Fe_2(SO_4)_3 \cdot xH_2O$ in 0.1 *M* sulfuric acid. Air-free solutions of ferrous perchlorate were prepared by adding iron powder to air-free perchloric acid in a screw cap bottle sealed with a neoprene gasket. The bottle was vented with a hypodermic needle to allow the escape of evolved hydrogen and allowed to stand for several hours. The bottle was then sealed by removing the needle and placed in a shaker for two or three days. Ferric-ferrous mixtures were prepared by removing oxygen from the ferric sulfate solution and adding the ferrous perchlorate solution. Air was excluded by preparing both solutions in sealed screw cap bottles and transferring the ferrous solution to the bottle containing the ferric iron through two six inch hypodermic needles connected by Tygon tubing, the ferrous perchlorate being forced through the tubing by nitrogen pressure. The ferrous content was determined by removing a 10-ml. sample and titrating it with standard dichromate. Another 10-ml. portion was reduced with stannous chloride and titrated with dichromate giving the sum of ferric plus ferrous.

All other chemicals were reagent grade and were not further purified.

Dissociation Constants of DHEG.—The dissociation constants of DHEG were determined by measuring with a glass electrode the *p*H of solutions of DHEG to which known amounts of standard acid or base had been added, and calculating the constants from the relations: $K_1 = [H^+]$ (moles base)/(moles DHEG − moles base). The hydrogen ion activity was converted to concentration by dividing it by the appropriate activity coefficient. At an ionic strength of 0.5, the concentration constants were measured as $K_1 = 10^{-2.50}$ and $K_2 = 10^{-8.11}$. Chaberek, Courtney and Martell[4] reported $pK_2 = 8.09$ at ionic strength 0.1.

Composite Ferric-Ferrous Waves at the Dropping Mercury Electrode in the Presence of DHEG.—Composite polarographic waves were measured in three supporting electrolyte solutions: 0.5 *M* potassium nitrate plus 0.05 *M* DHEG, 0.25 *M* sodium perchlorate plus 0.25 *M* DHEG and 0.5 *M* DHEG alone. A solution of 25% sodium hydroxide was added until its *p*H was slightly higher than that desired for the measurement. Twenty-five milliliters of this solution was placed in a polarographic cell, and air removed with nitrogen. A portion of air-free ferrous-ferric stock solution (0.5–1 ml.) was added to the solution in the cell and the current-voltage curve was recorded with a Sargent Model XXI polarograph. Significant points on the curve were also measured with a manual instrument. The electrode drop time was 5.0 seconds with the electrode short circuited, and "*m*" was 1.10 mg./second. All measurements were made at 25.0°. Potentials are reported versus the saturated calomel electrode (S.C.E.).

All solutions gave well defined composite waves with no discontinuity between the anodic and cathodic portions, indicating a reversible electrode reaction. The observed half-wave potentials are given in Table I. The slopes of the logarithmic plots varied between 0.06 and 0.08.

Potentiometric Measurement of the Ferric-Ferrous Potential in Excess of DHEG.—In order to extend the measurement of the oxidation potential of the ferric-ferrous-DHEG system to *p*H values in the acid region the potential was measured with a platinum wire indicator electrode. The two stock solutions used were 0.015 *M* in DHEG plus 0.50 *M* in sodium chlorate and 1 *M* in DHEG, respectively. Measurements were made by placing the DHEG solution in a polarographic cell whose top was covered with a thin sheet of rubber. The *p*H glass electrode, the platinum indicator electrode and the salt bridge to the saturated calomel electrode were inserted through holes in the rubber. After removing oxygen with nitrogen 0.5 ml. of ferric-ferrous stock solution was added. The *p*H of the solution was varied from 2.5 to 11 by the addition of small volumes of concentrated alkali. The data recorded in Fig. 1 refer to solutions equimolar in ferric and ferrous. The measured potential was corrected for the small variation from equimolarity with the aid of the Nernst equation.

TABLE I

HALF-WAVE POTENTIAL OF COMPOSITE FERRIC-FERROUS WAVES

Total iron concentration 3.9 millimolar

*p*H	Electrolyte	$E_{1/2}$ *vs.* S.C.E.
7.97	0.5 *M* KNO_3, 0.05 *M* DHEG	−0.238
8.43	.5 *M* KNO_3, .05 *M* DHEG	− .300
9.18	.5 *M* KNO_3, .05 *M* DHEG	− .403
11.88	.5 *M* KNO_3, .05 *M* DHEG	− .725
12.57	.5 *M* KNO_3, .05 *M* DHEG	− .822
8.56	.5 *M* DHEG	− .276
10.00	.5 *M* DHEG	− .446
12.42	.5 *M* DHEG	− .764
8.01	.25 $NaClO_4$, 0.25 *M* DHEG	− .222
10.60	.25 *M* $NaClO_4$, 0.25 *M* ($NaClO_4$ + NaOH), 0.25 *M* DHEG	− .554
12.35	.25 *M* $NaClO_4$, 0.25 *M* ($NaClO_4$ + NaOH), 0.25 *M* DHEG	− .778

TABLE II

APPARENT STABILITY CONSTANT OF $FeG(OH)_2$ IN ACID MEDIUM

$K_{III} = [FeG(OH)_2]/[Fe^{+3}][G^-][OH^-]^2$. Total [DHEG] is 0.015 *M* in 0.5 *M* $NaClO_4$

*p*H	*E* *vs.* S.C.E.	−log G^-	Apparent log K_{III}
2	0.47	8.72	(33.1)
3	.41	7.17	30.5
4	.25	6.05	30.1
5	.08	5.03	30.0
6	− .05	4.03	29.2

Electrode Reactions in the Ferric–Ferrous–DHEG System.—The general equation for the half-wave potential of a system in which both the oxidized and reduced forms are soluble is[5]

$$E_{1/2} = E^0 - (0.059/a)\log(k_{ox}/k_{red}) - ((p - q)/a)\ 0.059 \log C_x \quad (1)$$

where the electrode reaction is expressed by

$$MX_p + ae \rightleftarrows MX_q + (p - q)X \quad (2)$$

E^0 is the standard electrode potential of the system, C_x is the ligand concentration while k_{ox} and k_{red} are constants.

The iron–DHEG half-wave potential varies with *p*H, therefore hydroxyl ion (or hydrogen ion) enters into the electrode reaction and can be treated as a ligand. The general equation, at constant DHEG concentration, can then be expressed as: $E_{1/2}$ = constant − $(p - q)/a$ 0.059 *p*H. From a plot of the data in Table I the slope of the $E_{1/2}$ *vs.* *p*H plot at a given DHEG concentration is found to be −0.12. Considering that "*a*" is one for the reduction of ferric to ferrous, $(p - q)$ in the expression for the electrode reaction is 2.

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[3] We are indebted to Mr. Stanley Bruckenstein for performing this titration.

[4] S. Chaberek, Jr., R. Courtney and A. Martell, THIS JOURNAL, **75**, 2185 (1953).

[5] I. M. Kolthoff and J. J. Lingane, "Polarography," 2nd ed., Interscience Publishers, Inc., New York, N. Y., 1952, p. 218.

The plot of $E_1/_2$ *vs.* log concentration of DHEG at constant *p*H has a slope of about 0.05, indicating that $(p - q)$ for DHEG in neutral or alkaline solution is minus one. Thus, two hydroxyl ions are involved on the right side of the equation for the electrode process, and one uncomplexed DHEG on the left side. The simplest expression for such an electrode reaction is

$$\text{FeG(OH)}_2 + \text{G}^- + \text{e} = \text{FeG}_2 + 2\text{OH}^- \quad (3)$$

The potentiometric measurements show that different electrode reactions prevail below *p*H 7. The change in electrode reaction is strikingly demonstrated by the effect of DHEG concentration on the electrode potential. While an increase in DHEG concentration makes the potential more positive in alkaline solution, it makes the potential more negative in acid medium, indicating that DHEG occurs at the right side of the equation instead of at the left as in equation 3. The electrode reaction which predominates in the *p*H range 3–5 is probably: $\text{FeG(OH)}_2 + \text{e} = \text{Fe}^{+2} + \text{G}^- + 2\text{OH}^-$. In this *p*H range the ferrous complex is no longer stable, while at a *p*H smaller than[3] the ferric complex also becomes unstable. This is evidenced by the leveling off of the potential *versus* *p*H curve (Fig. 1) as the *p*H becomes smaller.

Stability Constants of the Ferric and Ferrous Complexes with DHEG.—In the *p*H range 3–5 where the ferric complex is reduced to the aquo ferrous ion, the stability constant of the complex FeG(OH)_2 can be calculated from the electrode potential. The following expression was derived from the Nernst equation

$$E = E^0 - 0.059 \log K_{\text{III}} + 0.118\, p\text{OH}^- - 0.059 \log [\text{G}^-] \quad (4)$$

where E is the measured electrode potential, E^0 the standard potential of the aquo ferric–ferrous couple, and K_{III} the stability constant of FeG(OH)_2

$$K_{\text{III}} = [\text{FeG(OH)}_2]/[\text{Fe}^{+3}][\text{G}^-][\text{OH}^-]^2 \quad (5)$$

The concentration of G^- was calculated from the total DHEG present by means of

$$[\text{G}^-] = C_{\text{DHEG}}/(1 + [\text{H}^+])/K_2 + [\text{H}^+]^2/(K_1K_2)$$

where K_1 and K_2 are the acid dissociation constants of DHEG, the concentration of the ferric–DHEG complex being negligible as compared to the total DHEG concentration. As the formal standard potential of the aquo ferric–ferrous couple a value of 0.49 volt *versus* S.C.E. at ionic strength of 0.5 was used.[6] The values calculated from the data in Fig. 1 at an ionic strength of 0.5 are given in Table II. The values of log K_{III} are reasonably constant in the range *p*H 3 to *p*H 5, which is the range in which the reduction of the complex to the aquo ferrous ion is the dominant reaction.

Since both the ferrous and ferric complexes are stable in alkaline medium, the ratio of their stability constants can be calculated from the oxidation potentials. Assuming that the reaction is represented by equation 3, an expression can be derived[7]

$$E^0_{\text{complex}} = E^0_{\text{aquo}} - 0.059 \log K_{\text{III}}/K_{\text{II}} \quad (6)$$

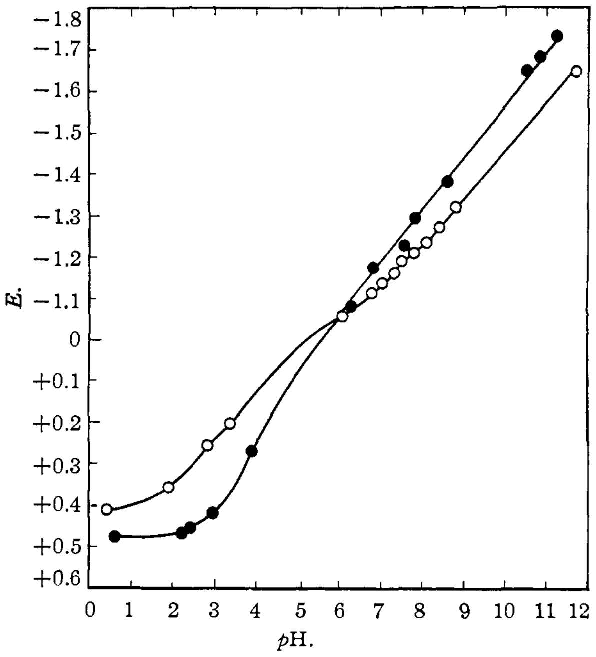

Fig. 1.—Effect of *p*H on oxidation potential of Fe(III)-Fe(II)-DHEG system measured with platinum electrode; [Fe(III)] = [Fe(II)] = 0.0017 *M*; ●, C_{DHEG} = 0.015 *M*, 0.5 *M* ClO_4^-; ○, C_{DHEG} = 1.0 *M*.

where $K_{\text{II}} = [\text{FeG}_2]/[\text{Fe}^{+2}][\text{G}^-]^2$. The standard potential of the iron–DHEG system, E^0_{complex}, was calculated from the data in Table I to be −0.94 volt *versus* S.C.E. E^0_{aquo} is the formal potential of the aquo ferric–ferrous couple. The ratio of the stability constants $(K_{\text{III}}/K_{\text{II}})$ was calculated to be $10^{24.2}$. Substituting $10^{30.1}$ for K_{III} gives $K_{\text{II}} = 10^{5.9}$.

Diffusion Current of Ferric–DHEG Solutions at the Dropping Electrode. Solubility of Ferric Hydroxide in the Presence of DHEG.—The presence of a red color in a number of solutions prepared to measure the diffusion current constant of ferric iron in excess of DHEG suggested that such solutions might be supersaturated in ferric hydroxide. Also the diffusion currents in such solutions were not well reproducible and depended upon time of standing after preparation. Measurements of the diffusion current of ferric–DHEG solutions were made after aging sufficiently to ensure the presence of an equilibrium state.

A number of solutions 4.14 millimolar in ferric iron were prepared, the DHEG concentration ranging from 0.005 to 0.5 *M*. All solutions were 0.5 *M* in sodium perchlorate, and some were 0.05 *M* in acetate or ammonia buffers. The solutions were made up in 120-ml. screw cap bottles sealed with a neoprene gasket beneath the cap. The bottles were placed in a 25° thermostat, and rotated end over end for one week. Samples were removed and the current voltage curves were recorded. The diffusion currents were measured manually and the *p*H of the solutions was measured. The samples were then returned to the bottles and rotated for 19 weeks more, after which the diffusion current and *p*H measurements were repeated. Results of the measurements are given in Table III.

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[6] W. Schumb, M. Sherrill and S. Sweetser, This Journal, **59**, 2360 (1937).

[7] Reference 3, p. 222.

TABLE III

EFFECT OF AGING ON THE APPARENT DIFFUSION CURRENT CONSTANT OF FERRIC-DHEG COMPLEX

$[Fe^{III}] = 4.14 \times 10^{-3} M$. I is diffusion current constant

[DHEG]	1 week after mixing I	1 week after mixing pH	20 weeks after mixing I	20 weeks after mixing pH
0.50	1.17	4.32	1.10	4.32
.50	1.25	8.5	1.10	8.49
.50	1.29	12.40	1.08	12.4
.05	1.21	4.16	1.06	4.18
.05	1.21	7.25	1.01	7.20
.05	1.26	7.60	1.14	7.52
.05	1.30	11.80	0.81	11.80
.005	0.04	4.10	.02	4.10
.005	.02	5.80	.01	6.74
.005	.02	8.47	.02	8.52
.005	.06	12.22	.01	12.2

The diffusion current constant of ferric iron in 0.5 M DHEG after 20 weeks of standing equaled 1.10 and was independent of pH between pH 4 and 12. In solutions 0.005 M in DHEG, the diffusion currents were the same order of magnitude as the residual current, indicating that essentially all of the iron had been precipitated as ferric hydroxide. In the intermediate case, where the DHEG concentration was 0.05 M, the apparent diffusion current constant had dropped to 0.8 at pH 11.8. Apparently the ferric–DHEG complex is stable in the latter solutions, but the ferric ion concentration is such that the solubility product of ferric hydroxide is very nearly exceeded or just exceeded. It may be mentioned that the drop in diffusion current constant is extremely slow and may be due to a very low association. Assuming that the low value of the diffusion current constant of 0.81 at pH 11.8 is due to partial precipitation of ferric hydroxide and that a state of equilibrium is attained, both the expression for the stability of the complex (equation 5) and the solubility product of ferric hydroxide must be satisfied. Using a value of the solubility product[8] of 6×10^{-38} and estimated values of activity coefficients yields a value of K_{III} of $10^{31.3}$ as compared to $10^{30.1}$ from potentiometric measurements. It is gratifying that the order of magnitude is the same considering that the solubility product of ferric hydroxide is not known accurately and changes with the age and composition of the precipitate.

Discussion

In a paper published after the completion of this work, Chaberek, Courtney and Martell[4] reported a ferric–DHEG complex essentially of the same composition as the one investigated by us. In the titration of DHEG with base in the presence of ferric iron, however, they found two inflections in the curve giving pH *versus* moles of base, the second of which they ascribed to the formation of a binuclear complex in the pH range 8–12 by the reaction: $3FeAO_2 + 3OH^- = Fe(OH)_3 + Fe(AO_2)_3^{-3}$, where $A(OH)_2^-$ corresponds to our G^-. Our work has shown that the electrode reaction for the reduction of the ferric complex follows $FeG(OH)_2 + G^- + e = FeG_2 + 2OH^-$ up to pH 11, so that if a binuclear complex is present, it must be in extremely rapid equilibrium with the $FeG(OH)_2$ form. The formation of ferric hydroxide called for by their equation was observed by Chaberek, *et al.*, but they did not report if the amount precipitated was $^1/_3$ of the total iron. Comparison of the stability constant of the complex with the solubility product of ferric hydroxide shows that ferric hydroxide is precipitated at high pH because its solubility product is exceeded, even in the presence of the DHEG complex. This is demonstrated by the results in Table III.

[8] W. M. Latimer, "Oxidation Potentials," 2nd Edition, Prentice-Hall, Inc., New York, N. Y., 1952, p. 224.

MINNEAPOLIS, MINN.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

The Stability of Iron(III)–Phenol Complexes[1]

BY RONALD M. MILBURN

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Equilibrium constants have been measured in aqueous solution at 25° for the reaction $Fe^{3+} + XC_6H_4OH \rightleftarrows XC_6H_4OFe^{2+} + H^+$, with X equal to H, p-CH_3, p-Br, p-NO_2 and m-NO_2. The importance of competing hydrolysis reactions is demonstrated. Equilibrium constants for the reaction $Fe^{3+} + XC_6H_4O^- \rightleftarrows XC_6H_4OFe^{2+}$ are calculated and compared to those for the reaction $H^+ + XC_6H_4O^- \rightleftarrows XC_6H_4OH$. The results are discussed in terms of Hammett's sigma constants. A simple electrostatic model is used to calculate equilibrium constants for the exchange reaction $XC_6H_4OFe^{2+} + C_6H_5O^- \rightleftarrows XC_6H_4O^- + C_6H_5OFe^{2+}$. The difference between calculated and observed values is a measure of the inadequacy of the simple model with localized charges.

A number of workers have investigated iron(III)–phenol complexes.[2–17] Taylor[5] and Broumand and

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[1] Part of this paper is taken from a thesis presented by Ronald M. Milburn in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Duke University.

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