TABLE III

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

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

[DHEG]	1 week after mixing *I*	1 week after mixing *p*H	20 weeks after mixing *I*	20 weeks after mixing *p*H
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 *p*H between *p*H 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 *p*H 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 *p*H 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 *p*H *versus* moles of base, the second of which they ascribed to the formation of a binuclear complex in the *p*H range 8–12 by the reaction: $3\mathrm{FeAO_2} + 3\mathrm{OH^-} = \mathrm{Fe(OH)_3} + \mathrm{Fe(AO_2)_3}^{-3}$, where $\mathrm{A(OH)_2}^-$ corresponds to our G^-. Our work has shown that the electrode reaction for the reduction of the ferric complex follows $\mathrm{FeG(OH)_2} + \mathrm{G}^- + e = \mathrm{FeG_2} + 2\mathrm{OH}^-$ up to *p*H 11, so that if a binuclear complex is present, it must be in extremely rapid equilibrium with the $\mathrm{FeG(OH)_2}$ 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 *p*H because its solubility product is exceeded, even in the presence of the DHEG complex. This is demonstrated by the results in Table III.

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[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

RECEIVED NOVEMBER 15, 1954

Equilibrium constants have been measured in aqueous solution at 25° for the reaction $\mathrm{Fe^{3+}} + \mathrm{XC_6H_4OH} \rightleftarrows \mathrm{XC_6H_4OFe^{2+}} + \mathrm{H^+}$, with X equal to H, *p*-$\mathrm{CH_3}$, *p*-Br, *p*-$\mathrm{NO_2}$ and *m*-$\mathrm{NO_2}$. The importance of competing hydrolysis reactions is demonstrated. Equilibrium constants for the reaction $\mathrm{Fe^{3+}} + \mathrm{XC_6H_4O^-} \rightleftarrows \mathrm{XC_6H_4OFe^{2+}}$ are calculated and compared to those for the reaction $\mathrm{H^+} + \mathrm{XC_6H_4O^-} \rightleftarrows \mathrm{XC_6H_4OH}$. 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 $\mathrm{XC_6H_4OFe^{2+}} + \mathrm{C_6H_5O^-} \rightleftarrows \mathrm{XC_6H_4O^-} + \mathrm{C_6H_5OFe^{2+}}$. 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.

[2] R. F. Weinland and K. Binder, *Ber.*, **45**, 2498 (1912); **46**, 874 (1913).

[3] M. Claasz, *Arch. Pharm.*, **253**, 360 (1915).

[4] E. F. Wesp and W. R. Brode, THIS JOURNAL, **56**, 1037 (1934).

[5] J. R. Taylor, *Virginia J. Sci.*, **3**, 24 (1942).

[6] J. H. Yoe and A. L. Jones, *Ind. Eng. Chem.*, *Anal. Ed.*, **16**, 111 (1944).

[7] A. K. Babko, *J. Gen. Chem.* (*U.S.S.S.R*), **15**, 874 (1945).

[8] A. L. Jones and L. B. Yeatts, THIS JOURNAL, **69**, 1277 (1947).

[9] A. E. Harvey and D. L. Manning, *ibid.*, **72**, 4488 (1950).

[10] H. Broumand and J. H. Smith, *ibid.*, **74**, 1037 (1952).

[11] S. Soloway and S. H. Wilen, *Anal. Chem.*, **24**, 979 (1952).

[12] S. Banerjee and B. C. Haldar, *Nature*, **165**, 1012 (1950).

[13] R. L. Herbst, R. H. Close, F. J. Mazzacua and R. F. Dwyer, THIS JOURNAL, **74**, 269 (1952).

[14] S. K. K. Jatkar and B. N. Mattoo, *J. Indian Chem. Soc.*, **30**, 592, 597 (1953).

[15] K. Sone, *Bull. Chem. Soc. Japan*, **26**, 467 (1953).

[16] Ch. Bobtelsky and S. Kertes, *Bull. soc. chim. France*, 143, 148 (1954).

[17] A. Ågren, *Acta Chem. Scand.*, **8**, 266, 1059 (1954).

Smith[10] have demonstrated that the $XC_6H_4OFe^{2+}$ ion is the principal species formed by monohydric phenols in aqueous solutions of low *p*H. A number of conflicting reports[12–15] are based on experiments in which such variables as *p*H, temperature and ionic strength were not controlled.

Equilibrium constants for reaction 1 are reported for X equal to H by Babko,[7] and for X equal to H, *o*-CH_3, *o*-CHO and *o*-$COCH_3$ by Jatkar and Mattoo.[14]

$$Fe^{3+} + XC_6H_4O^- \rightleftharpoons XC_6H_4OFe^{2+} \qquad (1)$$

Babko neglected the iron(III) ion removed by hydrolysis and phenolysis,[18] temperature was not recorded, no attempt was made to keep ionic strength constant or take activity coefficients into account, and measurements were not made until initially changing optical densities had become steady.[19] No corrections were made for acid produced by phenolysis.[20] Jatkar and Mattoo also disregarded temperature control, ionic strength and changing optical densities. Competing hydrolysis reactions and chloride complexes of iron(III) were also overlooked. More important, they neglected to control or have knowledge of hydrogen ion concentrations, and identified the phenolate ion concentration with the total introduced phenol in acidic solutions.[21]

We have measured equilibrium constants for reaction 2, with X equal to H, *p*-CH_3, *p*-Br, *p*-NO_2 and *m*-NO_2. Conditions were chosen where reactions 2 and 3 were the only important iron(III) equilibria

$$Fe^{3+} + XC_6H_4OH \rightleftharpoons XC_2H_4OFe^{2+} + H^+ \qquad (2)$$

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

Experimental[22]

Materials.—Water and standard solutions of perchloric acid, sodium perchlorate and iron(III) perchlorate, were prepared as previously described.[23] A stock 0.1002 *M* iron(III) perchlorate solution, 0.0122 *M* in perchloric acid, was used for the preparation of all other iron(III) solutions.

Phenol (Mallinckrodt analytical reagent) was purified by distillation (b.p. 98–98.5° at 37 mm.). Stock solutions were analyzed by the bromate method.[24] *p*-Cresol (Eastman Kodak Co.) was also purified by distillation (b.p. 88.5–89° at 10 mm.). *p*-Nitrophenol (Paragon Testing Laboratory), *m*-nitrophenol (Eastman Kodak Co.) and *p*-bromophenol (Eastman Kodak Co.) were recrystallized from chloroform (m.p. 113, 96 and 63°, respectively). Standard solutions of substituted phenols were prepared from weighed portions of the substances. Check titrations were made on the *p*-nitrophenol solution with standard sodium hydroxide, with thymolphthalein as indicator. Phenol and *p*-cresol solutions were used immediately after preparation.

Technique.—Optical densities were measured in 1-cm. quartz cells with a model DU Beckman spectrophotometer. A thermostat held the temperature of solutions at 25 ± 0.1°. Recorded optical densities were independent of the slit width. Test solutions were prepared by diluting the phenol with an equal volume of iron(III) perchlorate solution. The iron(III) solutions used, prepared from the stock solution, were allowed to mature for about five days before use for reasons previously outlined.[23]

In some cases knowledge of optical densities at 25° was required immediately after preparation of the test solution. The two constituent solutions, one containing the iron(III) with the required acid and sodium perchlorate, and the other containing the phenol, were brought to 25°, mixed, and immediately placed in a thermostated cell in the spectrophotometer. Optical densities were measured 30 seconds after mixing, and thereafter at intervals to enable extrapolation to zero time.

Method and Results.—Previous work[10,23,25] indicated that in sufficiently dilute aqueous iron(III) solutions of moderate acidity the only important hydrolysis and phenolysis equilibria would be reactions 2 and 3. By choice of wave length the optical density may be attributed to the $XC_6H_4OFe^{2+}$ ion alone. Under these conditions the following equations hold

$$k_1 = [FeOH^{2+}][H^+]/[Fe^{3+}] \qquad (4)$$

$$k_X = [XC_6H_4OFe^{2+}][H^+]/[Fe^{3+}][XC_6H_4OH] \qquad (5)$$

$$C_{Fe} = [Fe^{3+}] + [FeOH^{2+}] + [XC_6H_4OFe^{2+}] \qquad (6)$$

$$D = e_X[XC_6H_4OFe^{2+}] \qquad (7)$$

Brackets indicate concentrations, C_{Fe} is the total iron(III) concentration, D the total optical density for a 1-cm. cell, and e_X the absorption coefficient of the $XC_6H_4OFe^{2+}$ ion. Elimination of the concentration terms $[Fe^{3+}]$, $[FeOH^{2+}]$ and $[XC_6H_4OFe^{2+}]$ from equations 4–7 gives

$$1/D = (1/C_{Fe}e_X)\{1 + k_1/[XC_6H_4OH]k_X + [H^+]/[XC_6H_4OH]k_X\} \qquad (8)$$

By maintaining constant temperature, ionic strength and concentrations of total iron(III) and free phenol, a linear relation was obtained between $1/D$ and $[H^+]$. Values of k_X and e_X were calculated from the slopes and extrapolated intercepts for $[H^+] = 0$, using the equations

$$k_X = \{\text{intercept/slope} - k_1\}/[XC_6H_4OH] \qquad (9)$$

$$e_X = 1/C_{Fe}\{\text{intercept} - k_1(\text{slope})\} \qquad (10)$$

For each phenol optical densities were measured in the region of 550 mμ on a series of solutions of varying acidities. Each solution was 10^{-3} *M* in iron(III) and had an ionic strength of 0.027. All phenol concentrations were of the order of 0.05 *M*, except for phenol itself, for which more concentrated solutions were also studied. The concentrations of free phenolate ions must have been negligible, as for each phenol $pK_a > 7$, and for each solution $pH < 3$. The concentration of free phenol was held essentially constant and equal to the total phenol concentration by maintaining a constant total phenol concentration in large excess to the total iron(III) concentration.

As the colors formed by phenol and *p*-cresol faded, optical densities were extrapolated to zero time as already described. It was assumed that the extrapolated value would correspond to the complete establishment of equilibria 2 and 3 and to no oxidation–reduction reaction. The latter assumption must be true. A check was made on the rate of establishment of the hydrolysis and phenolysis equilibria. When water was substituted for the phenol, the optical density at 340 mμ had attained a constant value by the time the first measurement could be made, indicating rapid establishment of the hydrolysis equilibrium. The iron(III)-*p*-nitrophenol colors are relatively stable, optical densities remaining constant for a prolonged time. On using *p*-nitrophenol it was found that the equilibrium values had also been attained by the time the first measurement could be made. It has been assumed that the equilibria with phenol and *p*-cresol are also established rapidly.

Under the chosen conditions there was no appreciable absorption by the iron(III) ion, hydrolyzed iron(III) or phenols. This is required by equation 7 and hence by equation 8. A further requirement is that the $FeOH^{2+}$ ion be the only hydrolyzed species of importance. Previous work[23,25] indicated that the second hydrolysis could be neglected in all solutions, with the possible exception of the solution with lowest acidity in each series. An estimate can be made of the error introduced by neglecting dimerization

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[18] The phenol was in large excess over the iron(III).

[19] The initial change is caused by oxidation of the phenol and reduction of the iron(III). The reaction later proceeds more slowly, but continues until one of the reactants is consumed.

[20] Mention is made of correcting hydrogen ion concentrations for acid produced by hydrolysis, although no details are given.

[21] Solutions must have been acidic to prevent precipitation of iron(III) hydroxide.

[22] Melting points and boiling points are uncorrected.

[23] R. M. Milburn and W. C. Vosburgh, THIS JOURNAL, in press.

[24] "Scott's Standard Methods of Chemical Analysis," fifth edition, 1939, p. 2253.

[25] T. H. Siddall and W. C. Vosburgh, THIS JOURNAL, **73**, 4270 (1951).

of the $FeOH^{2+}$ ion. The dimerization constant for 25° and an ionic strength of 0.027 is 90.[22] From this we calculate that no more than 3% of the iron(III) would be dimerized in the solutions of lowest acidity. In more acid solutions the amount would be less. Neglect of reaction 3 would reduce equations 9 and 10 to k_X = (intercept)/(slope)[XC_6H_4OH] and $e_X = 1/C_{Fe}$(intercept). The equations give errors of the order of 100% in k_X and e_X. The importance of taking hydrolysis into account is evident.

Corrections were made for the small amounts of acid produced by hydrolysis and phenolysis. If α is the fraction of iron(III) hydrolyzed and β the fraction phenolyzed, the following equations hold, where h_0 is the introduced perchloric acid concentration and C_X the total phenol concentration (equal to the free phenol, as $C_X >> C_{Fe}$ and pH $<< pK_a$).

$$k_1 = \alpha C_{Fe}\{h_0 + (\alpha + \beta)C_{Fe}\}/C_{Fe}(1 - \alpha - \beta) \quad (11)$$

$$k_X = \beta C_{Fe}\{h_0 + (\alpha + \beta)C_{Fe}\}/C_X C_{Fe}(1 - \alpha - \beta) \quad (12)$$

Division of equation 12 by equation 11 gives $\beta = (C_X k_X/k_1)\alpha$. Substituting for β in equation 11 gives

$$\alpha^2 C_{Fe}\{1 + C_X k_X/k_1\} + \alpha\{h_0 + k_1 + C_X k_X\} - k_1 = 0 \quad (13)$$

Plots of $1/D$ against h_0 allowed preliminary estimates of k_X from equation 9, with $k_1 = 3.83 \times 10^{-3}$.[23] Substituting these values into equation 13, together with the known values of C_{Fe}, C_X, k_1 and h_0, allowed estimates of α and β for each solution. These gave the corrected acidity, $[H^+] = h_0 + (\alpha + \beta)C_{Fe}$. Plots of $1/D$ against $[H^+]$ gave final estimates of k_X. Further approximations lead to significant changes.

Plots of $1/D$ against $[H^+]$ for 550 mμ are shown in Fig. 1.

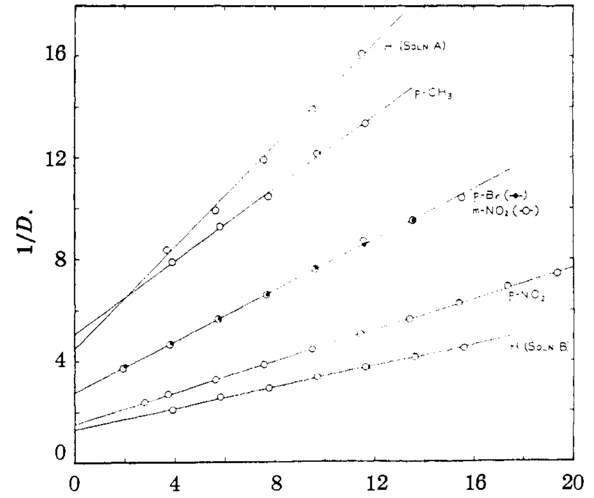

Fig. 1.—Evaluation of k_X, λ = 550 mμ, T = 25°, μ = 0.027, $C_{Fe} = 10^{-3}$ M. The slopes, a, and intercepts, b, of the least squares lines follow, with standard deviations in parentheses: X = p-CH_3, C_X = 0.0569 M, a = 5.05 (±0.18), b = 716 (±21); X = H, soln. A, C_X = 0.0518 M, a = 4.44 (0.26), b = 1002 (±32); soln. B, C_X = 0.255 M, a = 1.30 (±0.04), b = 207 (±3.5); X = p-Br, C_X = 0.0500 M, a = 2.77 (±0.03), b = 498 (±3); X = m-NO_2, C_X = 0.0400 M, a = 2.75 (±0.04), b = 500 (±4); X = p-NO_2, C_X = 0.0505 M, a = 1.51 (±0.02), b = 307 (±1). Results for other wave lengths, not indicated in figure: X = p-Br, λ = 565 mμ, C_X = 0.0500 M, a = 2.71 (±0.02), b = 495.6 (±2.4); X = m-NO_2, λ = 525 mμ, C_X = 0.0400 M, a = 2.48 (±0.04), b = 464 (±4); X = p-NO_2, λ = 525 mμ, C_X = 0.0505 M, a = 1.41 (±0.01), b = 284 (±1).

The concentrations of the phenols and the slopes and intercepts of the least squares lines are detailed beneath the figure. Results for other wave lengths are also given. Final values of k_X and e_X follow, with standard deviations in parentheses[26]; $k_{p-CH_3} = 5.7(\pm0.6) \times 10^{-2}$, $e_{p-CH_3} = 435(\pm40)$; $k_H = 0.96(\pm0.09) \times 10^{-2}$, $e_H = 1950(\pm200)$; $k_{p-Br} = 3.37(\pm0.11) \times 10^{-2}$, $e_{p-Br} = 1150(\pm50)$; $k_{m-NO_2} = 3.97(\pm0.20) \times 10^{-2}$, $e_{m-NO_2} = 1200(\pm75)$; $k_{p-NO_2} = 2.22(\pm0.11) \times 10^{-2}$, $e_{p-NO_2} = 3000(\pm250)$. The equation $\log k = \log k° - 2.04\ \mu^{1/2}(1 + 2.4\ \mu^{1/2})$, which gives the ionic strength dependence of k_1,[23] was used to extrapolate k_X to zero ionic strength. The values of $k°_X$ with standard deviations are: $k°_{p-CH_3} = 9.9(\pm1.0) \times 10^{-2}$; $k°_H = 1.67(\pm0.16) \times 10^{-2}$; $k°_{p-Br} = 5.86(\pm0.19) \times 10^{-2}$. $k°_{m-NO_2} = 6.90(\pm0.35) \times 10^{-2}$; $k°_{p-NO_2} = 3.86(\pm0.19) \times 10^{-2}$.

Discussion

As the substituent X affects the affinity of the phenolate ion for both the iron(III) ion and the proton, it is profitable to evaluate equilibrium constants for reaction 1. These constants, which we designate K_X, are given by k_X/K_a, where K_a is the acid dissociation constant of the phenol. With use of the phenol acid dissociation constants of Bordwell and Cooper[27] we obtain the following values for $K°_X$. Standard deviations are in parentheses.[28] $K°_{p-CH_3} = 1.8(\pm0.2) \times 10^9$, $K°_H = 159(\pm0.08) \times 10^8$, $K°_{p-Br} = 1.27(\pm 0.06) \times 10,^8$ $K°_{m-NO_2} = 1.65(\pm0.11) \times 10^7$, $K°_{p-NO_2} = 5.5(\pm0.4) \times 10^5$.

It is of interest to compare $K°_X$ with $1/K°_a$, the activity constant for the reaction

$$XC_6H_4O^- + H^+ \rightleftarrows XC_6H_4OH \quad (14)$$

In Fig. 2 we plot log $K°_X$ and log($1/K°_a$) against Hammett's values of sigma[29] (lines I and II, re-

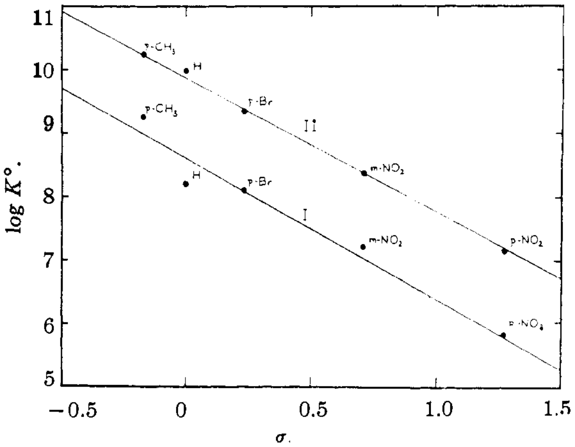

Fig. 2.—Relation of log $K°$ for reactions 1 and 14 with Hammett's sigma constants: I is the least squares line for reaction 1 (*i.e.*, $K° = K_X°$); $\rho = -2.20$; (log $K_H°$)$_{calcd.}$ = 8.60; standard deviation of points, $s = \pm0.30$; standard deviation of slope, $s_\rho = \pm0.26$. II is the least squares line for reaction 14 (*i.e.*, $K° = 1/K_a°$), calculated by Bordwell and Cooper[27] from their results on ten phenols; $\rho = -2.09$; (−log $K_a°$)$_{calcd.}$ for phenol = 9.86. From the results of Bordwell and Cooper we calculate $s = \pm0.10$; $s_\rho = \pm0.07$. Points corresponding to phenols studied by us are shown.

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(26) For the calculation of standard deviations, the standard deviation in k_1 was taken as 0.06×10^{-3}.[23]

(27) F. G. Bordwell and G. D. Cooper, THIS JOURNAL, **74**, 1058 (1952). Their Ka values refer to ionic strengths of less than 0.02. For present purposes this is sufficiently close to zero ionic strength. The values do not differ significantly from the $K°a$ values measured and estimated from the literature by Judson and Kilpatrick (*ibid.*, **71**, 3110 (1949)).

(28) For the calculation of standard deviations in $K°_X$, the standard deviations in log Ka were taken as ±0.02.

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

spectively). The slopes ρ for the least squares lines, with standard deviations, are: line I, $\rho = -2.20(\pm 0.26)$; line II, $\rho = -2.09(\pm 0.07)$. The similar values of ρ show that the substituents X have quantitatively similar effects of ΔF° for reactions 1 and 14. The scatter of points about line I is greater than would be expected from random errors; the standard deviation of points from line I is about ten times the average standard deviation in log K°_X.[30] The scatter could be accounted for by a dependence of ΔS° on X, or by potential energy terms of a type not operative for reaction 14 (for example, the O–Fe bond could have some double bond character).

Equilibrium constants for the proton exchange reaction 15 have been calculated by Judson and Kilpatrick[31] using the equation developed from electrostatic theory by Sarmousakis.[32]

$$XC_6H_4OH + C_6H_5O^- \rightleftarrows XC_6H_4O^- + C_6H_5OH \quad (15)$$

Parameters were adjusted to give agreement between calculated and observed values for *meta* derivatives. Differences between calculated and observed values for *para* derivatives were then calculated as a measure of resonance effects.

We have used the Sarmousakis equation to calculate K_H/K_X, the equilibrium constant for reaction 16.

$$XC_6H_4OFe^{2+} + C_6H_5O^- \rightleftarrows XC_6H_4O^- + C_6H_5OFe^{2+} \quad (16)$$

As far as possible the conventions were those used by Judson and Kilpatrick. An internal dielectric constant of 2.00 was used. The center of the dipole was taken as the mid-point of the line from the benzene ring to the projection of the outermost atom on the axis of the ring. Estimates of the focal radius, molecular cavity volume and interatomic distances were made from structural considerations.[33] For *m*-nitrophenol calculated and experimental values of K_H/K_X agreed for an effective charge on the iron atom of 0.86, with the C–O–Fe bond angle taken as 120°.[34,35] The same effective charge and C–O–Fe bond angle were used to calculate K_H/K_X for the *para* derivatives. Calculated and observed values of log K_H/K_X are: X = *p*-NO_2, calcd. = 0.73, obsd. = 2.46; X = *p*-Br, calcd. = 0.29, obsd. = 0.10; X = *p*-CH_3, calcd. = −0.06, obsd. = −1.05. The differences between calculated and observed values of log K for reactions 15 and 16 may be compared. Values of log($K_{\text{obsd.}}/K_{\text{calcd.}}$) are: reaction 15,[31] X = *p*-NO_2, 1.81; X = *p*-Br, −0.08; X = *p*-CH_3, −0.20; reaction 16, X = *p*-NO_2, 1.73; X = *p*-Br, −0.19; X = *p*-CH_3, −0.99. The differences are a measure of the inadequacy of the simple model with localized charge. The calculations take no account of the redistribution of charge through conjugation and polarization.

Acknowledgment.—I am very much indebted to Professor W. C. Vosburgh for many helpful discussions and for his continued interest in this work.

DURHAM, NORTH CAROLINA

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[30] The point for phenol itself, which lies furthest from the line, was checked carefully at two concentrations of phenol (0.255 and 0.0518 *M*) using both an analytical "Mallinckrodt" product that was not further purified, and a carefully fractionated sample. All four results agreed within the limits of experimental error. Similar results for two phenol concentrations may be regarded as evidence against polynuclear iron(III)-phenol species being important under the chosen conditions.

[31] C. M. Judson and M. Kilpatrick, THIS JOURNAL, **71**, 3115 (1949).

[32] J. N. Sarmousakis, *J. Chem. Phys.*, **12**, 277 (1944).

[33] The O–Fe bond distance was taken as 1.26 Å., the sum of the single bond covalent radius of the oxygen atom and the ionic radius of the iron(III) ion.

[34] The iron atom was assumed to be in the plane of the aromatic ring, *trans* to the nitro group. This configuration gives a slightly smaller repulsive charge–dipole interaction. However, the assumption of free rotation does not lead to significantly different results. For a C–O–Fe bond angle of 100°, calculated and experimental values agree for an effective charge of 0.75; for a bond angle of 180° an effective charge of 0.94 gives agreement.

[35] A small effective charge on the iron is in qualitative agreement with Pauling, *J. Chem. Soc.*, 1461 (1948), who considers that ionic charges are shared by solvating molecules.

[CONTRIBUTION FROM THE U. S. NAVAL RADIOLOGICAL DEFENSE LABORATORY]

Ion Exchange as a Separations Method. IX. Gradient Elution Theory[1]

BY EDWARD C. FREILING

RECEIVED SEPTEMBER 13, 1954

Ion-exchange column theory is applied to elutions made with both discontinuously and continuously graded eluants. Equations are derived for the resulting peak locations and peak widths. These equations are applied to a hypothetical example. The limitations of the theory are discussed.

Introduction

In the application of ion-exchange chromatography to the separation of a relatively large number of similar substances, such as the rare earths and amino acids, use of a constant strength of eluant does not permit the most efficient utilization of the time required for separation. For example, in separating the fission product rare earths, it is found that an eluant of relatively low concentration or *p*H is necessary to achieve good separation of Gd and Eu. Using the same eluant strength for the remainder of the run, however, one finds that the separation of the remaining rare earths is much greater than necessary. To reduce the time involved, recourse is frequently had to stepwise increases in eluant strength, as illustrated by the work of Ketelle and Boyd[1a] and Freiling and Bunney.[2] Stein and Moore[3] have successfully applied this technique to the separation of amino acids.

Gradient elution, *i.e.*, elution with a continuously

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[1] Paper presented before the Chemistry Division at the 121st Meeting of the American Association for the Advancement of Science, Berkeley, Calif., December, 1954.

[1a] B. H. Ketelle and G. E. Boyd, THIS JOURNAL, **69**, 2800 (1947).

[2] E. C. Freiling and L. R. Bunney, *ibid.*, **76**, 1021 (1954).

[3] W. H. Stein and S. Moore, *J. Biol. Chem.*, **192**, 663 (1951).