[Contribution from the Department of Chemistry, The Mount Sinai Hospital]

Fe(III) Complexes of *o*-Hydroxy Aromatic Acids[1]

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The complexes formed between Fe(III) and the three *o*-hydroxynaphthoic acids, 1-hydroxy-2-naphthoic (1:2), 2-hydroxy-1-naphthoic (2:1), 2-hydroxy-3-naphthoic (2:3), and salicylic acid(S.A.) at a *p*H of 2, 1.5 and 1 in 50% methanol–water as solvent have been investigated. The nature and stability constants of the complexes have been determined at $\mu = 0.2$ and 25°. The ionization constants of the acids, in the same solvent, are reported. The relationship between the iron, complexes, the ionization constants and the cyclic "transition state," postulated in the hydrolysis of the corresponding phosphoric acid esters, is discussed.

Our studies[2] on the mechanism of the hydrolysis of the phosphoric acid esters of the three *o*-hydroxynaphthoic acids: 1-hydroxy-2-naphthoic acid (1:2), 2-hydroxy-1-naphthoic acid (2:1) and 3-hydroxy-2-naphthoic acid (2:3) and salicylic acid (S.A.), suggested that an analogy might be drawn between the Fe(III) complex of the parent acid and the cyclic "transition state" postulated in the hydrolysis. It was also of interest to compare the acidities of these acids, not previously determined, with the stability constants of their Fe(III) complexes. A discussion of the various relationships and the nature of the complex is given below.

Complex formation between Fe(III) and the three hydroxynaphthoic acids as evidenced by the formation of a blue color has long been noted.[3a,b] However, the composition, stability and nature of these complexes has received little attention. In contrast the iron complexes of the benzenoid type, salicylic acid,[4,5a] and sulfosalicylic acid[5a,b,c,d] have been investigated over a wide *p*H range. In the acid region *p*H 1–2.5, it has been established that the latter two acids from 1:1 complexes with Fe(III) while at higher *p*H's (3–7) the composition of the complexes has been but recently elucidated by Ågren[5a] (*cf.* 5 c,d). Earlier work[5b] is not in agreement with that of Ågren.

Experimental

Solutions.—For the *p*H determinations a Cambridge research model *p*H meter was employed.[6] Because of the insolubility of the *o*-hydroxynaphthoic acids in water, 50% methanol solution (equal vol. methanol–water), which was either 0.2 or 0.1 molar in sodium perchlorate was used as solvent. Stock solutions of these solvents were prepared by exactly neutralizing the requisite amount of perchloric acid with standard alkali, adding an equal volume of methanol and diluting appropriately with a 50% methanol–water solution. The 0.2 *M* perchlorate solution at the *p*H's of 2 and 1.5, and the 0.1 *M* perchlorate at *p*H of 1 was used as solvent. A stock solution of iron perchlorate (0.08950 *M*) in water was prepared essentially according to R. C. Anderson[5b] and allowed to stand for a few days.[7] The final concentrations of the iron solutions at the desired *p*H were made by diluting the requisite amount of iron stock solution with the stock methanol–water solution and adjusting the *p*H with perchloric acid. These latter solutions were freshly made for each experiment, since the Fe(III) solutions (methanol–water) deteriorated slowly on standing. The volume of iron stock was insignificant as compared to the final volume, so that for solutions of *p*H *ca.* 2, 1.5 and 1 the final ionic strength was *ca.* 0.21, 0.23 and 0.20, respectively. The 2:1 acid, m.p. 198–200°, and the 2:3 acid, m.p. 220–221°, were prepared by the hydrolysis of the corresponding purified phosphates[2]; the 1:2 acid, m.p. 178°, was prepared as previously described,[2] the salicylic acid (Eastman Kodak Reagent Grade Chemicals) was recrystallized from water. The required concentration and *p*H of the acid solutions were obtained by dissolving the requisite amount of acid in the (methanol–water) stock solution and by adjusting the *p*H as described above.

Spectroscopic Determinations.—Optical densities were measured in one cm. matched quartz cells with a model DU Beckman spectrophotometer. A thermostat maintained the temperature of solutions at 25 ± 0.3°. For the measurement of stability constants concentrations were employed, when feasible, for which the optical density readings varied between *ca.* 0.3 and 0.7. The blank solution was in all cases the stock methanol–water solution. The general properties of the complexes were first ascertained prior to the more quantitative work. All four acids on admixture with iron solution developed full color almost immediately. The spectra of these complexes are given in Fig. 1. The 1:2, 2:1, 2:3 and S.A acids show the following $\lambda_{\max}$, respectively, 630, 590, 600 and 540 mμ. The colors are stable for at least an hour, providing the solutions are kept in the dark. Whereas, for example, in a solution containing equimolar quantities of the 2:3 acid and iron at *p*H *ca.* 2, the intensity of the color decreases at the rate of 0.75% per hr. in the dark, the rate of bleaching rises in diffuse daylight to 3.7% per hr. The sensitivity of the complexes to acidity is very apparent. Thus, at *p*H below *ca.* 0.5 nearly colorless solutions are obtained on mixing iron with the acids, while at *p*H *ca.* 3 and above a yellow-orange coloration is produced. At *p*H's from 1–2.4 the spectra of the complexes were the same, the difference lying only in the intensity of the absorption. In view of these observations the stability of the complexes was investigated at *p*H *ca.* 1, 1.5 and 2; the final solutions of acid and iron were freshly prepared in a darkened room and the absorbancies of the mixtures were determined within 5–15 min. after mixing.

Composition of Complexes.—The composition of the complexes was determined by the method of Job[8] at *p*H *ca.* 1, 1.5 and 2. The wave lengths chosen were $\lambda_{\max}$, $\lambda_{\max} - ca.$ 30 mμ, and $\lambda_{\max} - ca.$ 80 mμ. A plot of *D* (observed density minus density reading that would be observed if no complex were formed) against the ratio Fe/(acid + Fe) showed a maximum at 0.5, indicating that the complexes were of a 1:1 nature. In Fig. 2 a representative plot is given. The absorption of iron and of the acid at the wave lengths chosen were insignificant (see Fig. 2).

The molar absorbancy index, a_M, for each of the complexes was ascertained at the wave lengths employed in the determination of the stability constants. A known con-

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[1] This work was supported in part by a grant from the National Science Foundation.

[2] J. D. Chanley, E. M. Gindler and H. Sobotka, This Journal, **74**, 4347 (1952); J. D. Chanley and E. M. Gindler, *ibid.*, **75**, 4035 (1953).

[3] (a) "Elsevier Encyclopedia of Organic Chemistry," Series III, Vol. 12B, Elsevier Publishers, Co., New York, N. Y., 1953, pp. 4250, 4281, 4302. (b) These acids will be referred to hereinafter as the (1:2), (2:1), (2:3) and (S.A.) acids, as indicated above.

[4] A. K. Babko, *J. Gen. Chem. U.S.S.R.*, **15**, 754, 758 (1945); *C. A.*, **40**, 7042 (1947).

[5] (a) A. Ågren, *Acta Chem. Scand.*, **8**, 266, 1059 (1954); (b) R. T. Foley and R. C. Anderson, This Journal, **70**, 1195 (1948); **72**, 5609 (1950); (c) C. Banks and J. Patterson, *ibid.*, **73**, 3062 (1951); (d) M. Kennard and C. Johnson, *Proc. Trans. Texas Acad. Sci.*, **27**, 45 (1944).

[6] Our measurements of *p*H are essentially activity measurements (*pa*H); *cf.* R. G. Gates, *Chem. Revs.*, **42**, 1 (1948). Activities are indicated by parentheses ( ).

[7] T. H. Siddall and W. C. Vosburgh, This Journal, **73**, 4270 (1951).

[8] P. Job, *Ann. Chim.*, [10] **9**, 113 (1928); 97 (1936).

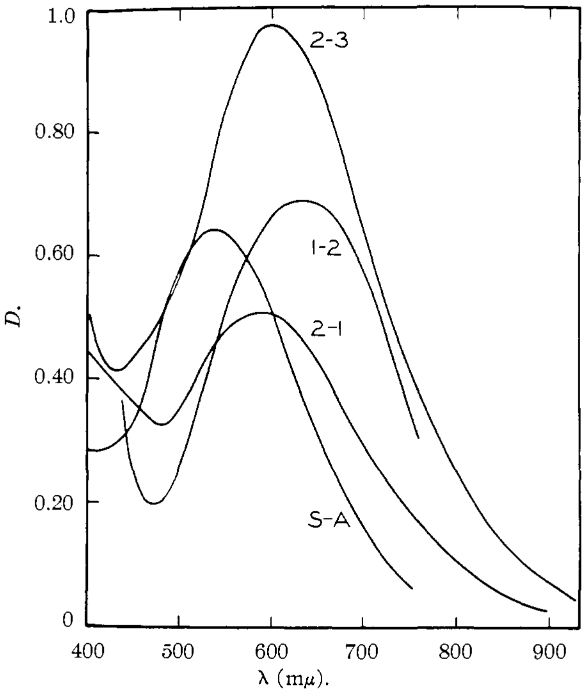

Fig. 1.—Spectra of Fe(III) complexes of 1-hydroxy-2-naphthoic (1:2), 2-hydroxy-1-naphthoic (2:1), 2-hydroxy-3-naphthoic (2:3), and salicylic (S.A.) acids for initial concentration of $[Fe^{3+}]$ = [acid] = 0.590×10^{-3} in 50% methanol–water solvent at *p*H 2.3. *D* is the observed optical density reading.

centration of acid (about the concentration used to determine stability constants) was treated with various excesses of iron solution at the same *p*H. A plot of observed density minus correction for iron absorption *vs.* concentration of iron indicated constancy in transmission at *p*H 2 when iron was *ca.* 20–35 times in excess of acid. The same a_M (±1%) was obtained using at least two concentrations of acid at *p*H of 2 and a third concentration at *p*H of 1. The molar absorbancy indexes found for the complexes 1:2, 2:1, 2:3 and S.A. acids with Fe(III) were 1480, 1280, 2340 and 1590, at the wave lengths 630, 590, 600 and 540 mμ, respectively. Having established the excess iron concentration necessary to form the complex completely, in each instance, for any concentration of acid, Beer's law was checked and found to hold.

Experimental Stability Constants.—These constants were derived, for the particular *p*H, from the experimental data. Thus, K_{exptl} is defined as

$$K_{\text{exptl}} = \frac{[\text{complex}]}{[[\text{Fe}^{3+}]_t - [\text{complex}]][[\text{H}_2\text{A}]_t - [\text{complex}]]}$$

$$[\text{complex}] = \text{concn. of colored material} = D_{\text{obsd}}/a_M l$$

where a_M = molar absorbancy index for the particular complex, D_{obsd} = observed optical density reading, l = 1 cm. in all instances, $[Fe^{3+}]_t$ = total concn. of Fe(III), $[H_2A]_t$ = total concn. of hydroxy acid.

At *p*H's of 2, 1, 5 and 1 the acids exist in the non-dissociated form completely. Listed in Table I are the various total concentrations of Fe(III) and acid used at the particular *p*H, and the experimentally determined concentration of complex formed. From these data the stability constants (K_{exptl}) have been determined. It is apparent that the value for K_{exptl} at *p*H of 1.5 is essentially constant for all mixtures, whereas at *p*H of 2 K_{exptl} showed a drift toward larger values, when one species was in great excess over the other. It can be demonstrated that in mixtures containing the same total concentrations of iron and acid, K_{exptl} may be most accurately evaluated, when the concentrations of the two constituents are equal. For this reason we have chosen at *p*H of 2 those values of K_{exptl}, calculated from solutions of nearly equivalent concentration of iron and acid.

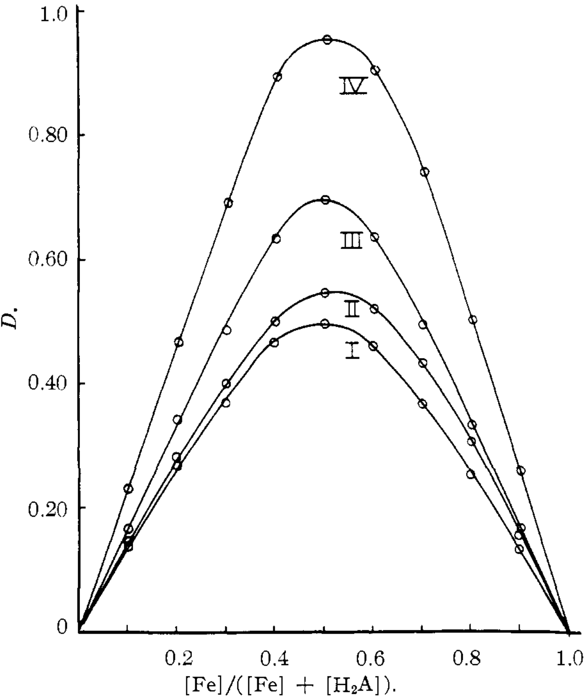

Fig. 2.—Job's method of continuous variations. $\bar{D}$, observed optical density reading minus reading, if no complex were formed, against mole fraction of Fe(III) in the mixture. In all cases, concentration of acid plus iron = 1.181×10^{-3}, *p*H 2.3, 50% methanol–water solvent. I, II, III and IV are the Fe(III) complexes of 2-hydroxy-1-naphthoic (λ 600 mμ), salicylic (λ 590 mμ), 1-hydroxy-2-naphthoic (λ 610 mμ), and 2-hydroxy-3-naphthoic (λ 600 mμ) acids, respectively. O represents experimental points.

The average values for the stability constants are listed in Table II.

The ionization constants of all four acids were determined in 50% methanol–water at 25° and μ = 0.2 by the method previously described.[2] The ionization constants of their acetates at total concentration of acid equal to 0.01 *M* were likewise determined in 50% methanol–water solution. The *pK*'s are listed in Table II.

Discussion

It is reasonable to presuppose that a single relationship exists between K_{exptl} and the true *K* or *K*'s for all four acids. The following significant equilibria[9] may be assumed and are defined under our experimental conditions by the accompanying equations

$$(1)\quad \text{Fe}^{3+} + \text{H}_2\text{A} \rightleftharpoons \text{FeHA}^{2+} + \text{H}^+$$

$$K_1 = \frac{[\text{FeHA}^{2+}](\text{H}^+)}{[\text{Fe}^{3+}][\text{H}_2\text{A}]}$$

$$(2)\quad \text{FeHA}^{2+} \rightleftharpoons \text{FeA}^+ + \text{H}^+$$

$$K_2 = \frac{[\text{FeA}^+](\text{H}^+)}{[\text{FeHA}^{2+}]}$$

$$(3)\quad \text{Fe}^{3+} + \text{H}_2\text{A} \rightleftharpoons \text{FeA}^+ + 2\text{H}^+$$

$$K_3 = K_1K_2 = \frac{[\text{FeA}^+](\text{H}^+)^2}{[\text{Fe}^{3+}][\text{H}_2\text{A}]}$$

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[9] The equilibrium $2\text{Fe}^{3+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Fe}_2(\text{OH})_2^{4+} + 2\text{H}^+$ is omitted. We assume that the dimerization constant of Fe(III) in methanol-water solution is of the same order of magnitude as in water, in which case it may be shown that at the acidities, low concentration of Fe(III) and the ionic strength used an insignificant amount of dimer may be expected, *cf.* R. M. Milburn, THIS JOURNAL, **77**, 2064 (1955); L. N. Mulay and P. W. Selwood, *ibid.*, **77**, 2693 (1955); R. M. Milburn and W. C. Vosburgh, *ibid.*, **77**, 1352 (1955).

TABLE I.

EXPERIMENTAL STABILITY CONSTANTS (K_{exptl})

pH	[Acid]$_t$[a]	[Fe]$_t$[a]	[Complex]$_e$[a]	$K_{\text{exptl}} \times 10^{-4}$
	1-Hydroxy-2-naphthoic acid			
1.97	9.666	1.074	1.004	(1.66)[b]
	7.518	3.222	2.797	1.39
	6.444	4.296	3.410	1.27
	5.270	5.370	3.740	1.41
	4.296	6.444	3.484	1.45
	2.148	8.592	2.001	(2.07)[b]
			Av.	1.36 ± 0.09
1.50	8.950	8.950	4.313	0.201
	10.74	7.160	4.090	.200
	7.160	10.74	4.100	.202
	14.32	3.580	2.493	.194
	3.580	14.32	2.577	.218
	1.790	16.11	1.368	.220
			Av.	0.206 ± 0.009
1.00	8.950	8.950	1.782	0.0347
	10.74	7.160	1.739	.0356
	7.160	10.74	1.688	.0340
	13.43	13.43	3.444	.0346
	16.11	10.74	3.309	.0347
	10.74	16.11	3.369	.0359
			Av.	0.349 ± 0.006
	2-Hydroxy-3-naphthoic acid			
1.98	5.370	5.370	3.152	0.641
	6.444	4.296	2.954	.631
	4.296	6.444	2.956	.632
	1.074	9.666	0.9435	(.829)[b]
	3.580	3.580	1.861	.630
	4.296	2.864	1.750	.617
	2.864	4.296	1.759	.627
	1.432	5.728	1.091	(.690)[b]
			Av.	0.630 ± 0.005
1.50	8.950	8.950	2.953	0.0821
	10.74	7.160	2.820	.0820
	7.160	10.74	2.781	.0798
	14.32	3.580	1.836	.0843
	3.581	14.32	1.814	.0822
	1.790	16.11	0.9842	.0808
	7.160	7.160	2.118	.0833
	8.592	5.728	2.011	.0822
	5.728	8.592	2.011	.0822
	11.46	2.864	1.324	.0849
	2.864	11.46	1.348	.0879
	1.432	12.89	0.7296	.0854
			Av.	0.0831 ± 0.002
1.00	13.43	13.43	1.391	0.00960
	16.11	10.74	1.374	.00995
	10.74	16.11	1.352	.00976
			Av.	0.00977 ± 0.00012
	Salicylic acid			
1.96	5.370	5.370	3.019	0.546
	6.444	4.296	2.827	.532
	4.296	6.444	2.830	.534
	1.074	9.666	0.903	(.601)[b]
			Av.	0.537 ± 0.006
1.50	8.950	8.950	2.767	0.0724
	10.74	7.160	2.657	.0730
	7.160	10.74	2.632	.0716
	14.32	3.580	1.742	.0754
	3.58	14.32	1.729	.0742
	1.79	16.11	0.956	.0756
			Av.	0.0736 ± 0.0014
1.03	17.90	17.90	2.390	0.00993
	21.48	14.32	2.330	.0101
	14.32	21.48	2.336	.0102
			Av.	0.0101 ± 0.0001
	2-Hydroxy-1-naphthoic acid			
1.96	5.370	5.370	2.689	0.374
	6.444	4.296	2.537	.369
	4.296	6.444	2.537	.369
	1.074	9.666	0.8744	(.498)[b]
			Av.	0.371 ± 0.002
1.51	10.740	10.74	3.091	0.0528
	12.888	8.592	2.935	.0521
	17.184	10.74	2.935	.0520
	4.298	17.18	1.948	.0544
	2.148	19.33	1.073	.0548
			Av.	0.0532 ± 0.0010
0.98	17.900	17.90	1.975	0.00806
	21.360	14.24	1.975	.00820
	14.240	21.36	1.963	.00814
			Av.	0.00813 ± 0.00005

[a] All concentrations are multiplied by 10^4; $[\,]_t$ = total concn. of acid or Fe(III); $[\,]_e$ = equilibrium concn. of complex. [b] Not included in average (see Experimental section).

$$\text{(4)}\quad \mathrm{Fe^{3+} + H_2O \rightleftarrows FeOH^{2+} + H^+} \qquad K_4 = \frac{[\mathrm{FeOH^{2+}}](\mathrm{H^+})}{[\mathrm{Fe^{3+}}]}$$

$$\text{(5)}\quad \mathrm{Fe^{3+} + CH_3OH \rightleftarrows FeOCH_3{}^{2+} + H^+} \qquad K_5 = \frac{[\mathrm{FeOCH_3{}^{2+}}](\mathrm{H^+})}{[\mathrm{Fe^{3+}}]}$$

where H_2A refers to the particular hydroxy acids. The assumption that only one complex, FeHA or FeA, is formed implies that the true K would be defined by equation 1 (K_1) in the first instance or equation 3 (K_3) in the second. Then to a first approximation (neglecting hydrolysis) one, but not both of the following, would be true: either K_{exptl} (at each pH) multiplied by (H) (equation 1) or by $(\mathrm{H})^2$ (equation 3) should give nearly constant values. This is not the case, even approximately, for any of the acids when K_{exptl} is multiplied by (H); while only for the 2:3 and S.A. acids, as will be shown subsequently, is equation 3 (K_3) applicable.

The assumption that both FeHA and FeA are present in the mixtures, but only one species is colored, predicts that K_{exptl} would not have a constant value, at a particular pH, when different initial concentrations of Fe(III) and hydroxy acid are used. Furthermore, it implies that a constant molar absorbancy index would not be found when the pH of the solution and initial concentrations of the hydroxy acid were varied. Both these implications are contrary to our findings. However, if we first assume that both FeA and FeHA are colored

TABLE II

STABILITY CONSTANTS (K_1, K_3) AND IONIZATION CONSTANTS (pK_A)

Acid	pH	$K_{\text{exptl}} \times 10^{-4}$	$K_{\text{calcd}} \times 10^{-4}$	K_1	K_3	pK_A[a]	$k_2 \times$ hr.$^{-1}$ [c]
2:3	1.98	0.630			(0.93)[d]		
	1.50	.0831			(.93)[d]	3.43(4.73)[b]	0.203
	1.00	.00977			.99		
S.A.	1.96	0.537			.857		
	1.50	.0736			.819	3.70(4.72)[b]	0.370
	1.03	.0101			.914		
					0.86 ± 0.05		
1:2	1.97	1.36	1.23				
	1.50	.206		19.3	1.68	3.75	1.41
	1.00	.0349					
2:1	1.96	.371	0.297				
	1.51	.0532		4.71	0.421	3.82(4.75)[b]	0.0109
	0.98	.00813					

[a] The pK_A of the parent hydroxy acids. [b] pK of the corresponding acetate, in parentheses. [c] k_2 is the specific rate constant for the hydrolysis of the phosphate ester at 37°, *cf.* ref. 5. [d] Calculated from data at pH 1.98 and 1.50.

and may be present in the mixtures, then, since the same molar absorbancy is obtained, FeA and FeAH must each have the same (or very nearly so) absorbancy at the wave lengths chosen for study. Under the last assumption (and its corollary) the constancy of K_{exptl} is to be expected, and the experimental findings may be accounted for. It should be noted that since FeA is derived from FeHA, Job's method of continuous variations would still indicate a 1:1 complex. The relationship between K_{exptl} and the true K's may now be deduced from the considerations

$$[\text{Fe}]_t = [\text{Fe}^{3+}]_e + [\text{FeHA}^{2+}]_e + [\text{FeA}^+]_e + [\text{FeOH}^{2+}]_e$$

$$[\text{H}_2\text{A}]_e = [\text{H}_2\text{A}]_t - [\text{FeHA}^{2+}]_e - [\text{FeA}^-]_e$$

Substituting for FeOH^{2+} and FeOCH_3^{2+}, $[\text{Fe}^{3+}]_e \times (K_4/(\text{H}^+))$ and $[\text{Fe}^{3+}]_e \times (K_5/(\text{H}^+))$, respectively, rearranging terms and combining K_4 and K_5 to give K^* (over-all hydrolysis constant) we have

$$[\text{Fe}^{3+}]_e = \frac{[\text{Fe}]_t - [\text{FeHA}^{2+}]_e - [\text{FeA}^+]_e}{1 + K^*/(\text{H}^+)}$$

Complex = $[\text{FeA}^+] + [\text{FeHA}^{2+}]$; $[\ ]_t$ = total concn.; $[\ ]_e$ = equilibrium concn.; ( ) = activity; omitting charge, then

$$K_{\text{exptl}} = \frac{[\text{FeHA} + \text{FeA}]_e}{[[\text{Fe}]_t - [\text{FeAH} + \text{FeA}]_e][[\text{H}_2\text{A}]_t - [\text{FeHA} + \text{FeA}]_e]}$$

and it may be shown that

$$K_{\text{exptl}} \times \left[1 + \frac{K^*}{(\text{H})}\right] = \frac{K_1}{(\text{H})} + \frac{K_3}{(\text{H})^2} \qquad (6)$$

Equation 6 predicts that the ratio of $K_{\text{exptl}} \times [1 + K^*/(\text{H})]\,(\text{H})^2$ for any pair of acids (6 in all) taken at the same pH[10] would give a constant value under either of two conditions: (a) the ratio of $K_1:K_3$ for each of the acids in the pair is the same, or (b) $K_3/(\text{H})^2 >> K_1/(\text{H})$ at all pH's. The latter condition simply means that (FeHA) is present (if at all) in an insignificant quantity as compared to FeA. On examination of these ratios at the three pH's studied, only the pair 2:3/S.A. gave constancy, 1.07, 1.13, 1.11, while a nearly constant ratio was found for the 2:1/1:2 pair; (0.280, 0.251, 0.252). However, for the four remaining pairs the ratio was nearly the same at pH *ca.* 2 and 1.5 (the great change coming when comparison was made at pH of 1). This indicated that for pH's of 2 and 1.5 the term $K_3/(\text{H})^2 > K_1/(\text{H})$, and suggested that for one of the pairs 2:3/S.A. or 2:1/1:2 (but not both) the equation relating K_{exptl} to the true K's could be reduced to

$$K_{\text{exptl}} \left[1 + \frac{K^*}{(\text{H})}\right] = \frac{K_3}{(\text{H})^2} \qquad (7)$$

The reduced equation adequately accounted *only* for the experimental findings for the 2:3 and S.A. acids. On solving for K^* from the data at pH 2 and 1.5 for 2:3 acid, the reasonable value[6-9] of 3.58×10^{-3} was obtained with $K_3 = 0.93$ the calculated value for K_3 from the experimental findings at pH of 1 was 0.99 (see Table II). Furthermore, substitution of the found value for K^* into the reduced equation and solving for K_3 in the case of S.A. gave at pH's 1.96, 1.50 and 1.03 the following values: 0.86, 0.82, 0.91, respectively. These variations are within the accuracy of pH determinations. For the 1:2 and 2:1 acids the reduced equation could not be employed. With K^* known, K_1 and K_2 were evaluated from the data at pH of 1.5 and 1 (hydrolysis being less important at these lower pH's). Substitution of these values for K_1 and K_2 at pH of 2 gave good agreement with the K_{exptl} values (see Table II). Small errors in pH measurement (±0.02 unit) would greatly affect the calculation at pH *ca.* 2. The K_1/K_3 ratio for the 1:2 and 2:1 acid were as predicted nearly identical, 11.5 and 11.2, respectively. We are in agreement with Ågren,[5a] who employed what is equivalent to our reduced equation in the analysis of complex formation between S.A. and Fe(III) (water as solvent, pH range 1.3–1.95).[11] It is conceivable that even with salicylic acid, at sufficiently high acidities the term $K_1/(\text{H})$ may no longer be insignificant as compared to $K_3/(\text{H})^2$. While the structure of the (FeHA) complex cannot be deduced from the data, it is

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(10) Our pH's are sufficiently close to permit this comparison, since the greatest variation in pH (at pH *ca.* 2) is but 0.02 unit and this would not seriously affect the term $(1 + K^*/(\text{H}))$, while at pH of 1 and 1.5, $K^*/(\text{H})$ would be expected to be much smaller than 1.

(11) Ågren considers the equilibria $\text{Fe}^{3+} + (\text{HA})^- \rightleftarrows \text{FeA}^+ + \text{H}^+$, this constant is equivalent to our $K_3 \times K_a$ (K_a is the ionization constant of the hydroxy acid).

apparent that the FeA complex is the inner salt complex (see Fig. 3B).

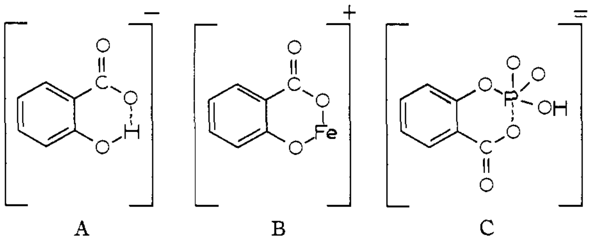

Fig. 3.—A, B and C are meant to represent the anion of the hydroxy acid, the Fe(III) complex (FeA), and the postulated "transition state" in the hydrolysis of the phosphate, respectively, for all four acids, and are illustrated by the specific case of salicylic acid.

The enhanced acid strength of the *o*-hydroxy-substituted naphthoic acids, as is true in the case of the salicylic acid,[12] may be ascribed to the stabilization of the anion (see Fig. 3A) by internal hydrogen bonding. That this explanation is in essence correct is evident from an examination of the acid strengths of the corresponding acetates (Table II), where no internal hydrogen bonding is possible. Not only is the acidity reduced in the latter cases, but is the same for the analogous acids. This latter finding would presuppose that the strongest of the *o*-hydroxy acids would be the one whose derived anion has the greatest tendency for hydrogen bonding. Hunsberger[13] has examined the infrared spectra of a large number of *o*-substituted α- and β-naphthol derivatives and has found that hydrogen bonding is stronger in the (1:2 = 2:1) substituted derivatives than in the 2:3 derivatives. The latter author has correlated these findings with the greater double bond character of the 1:2 position in the naphthalene ring. On the basis of the above one would conclude that the 2:3 acid should be the weakest acid in the naphthalene series. Actually it is found to be the strongest acid. No ready explanation can be given for the observed acid strength 2:3 > salicylic > (2:1 = 1:2). It would appear that other factors are involved. The fact that the anion of the 2:3 acid is yellow while those of the two other naphthoic acids are colorless suggests that (in addition to hydrogen bonding) this anion is stabilized by other means; the acidities of the 2:1 and 1:2 hydroxynaphthoic acids are on the other hand almost equivalent as would be predicted from the work of Hunsberger.[13]

The formal analogy in the structure of the Fe(III) complexes, the hydrogen bonded anions of the acids, and the postulated "transition state" (Fig. 3B) in the hydrolysis of the phosphate is evident (see Fig. 3). There is no obvious relationship between the ionization constants of the parent acids and the stability constants of their respective iron complexes. It has been pointed out by Martell and Calvin[14] that other factors, steric and resonance, markedly influence chelate formation. There appears to be no relationship between the acidities of the parent acids and the hydrolysis rates of the corresponding phosphoric acid esters. However, at least in so far as the naphthalene series are concerned, the order of the rates of hydrolysis of the phosphate esters (1:2 > 2:3 > 2:1) corresponds to the order of the stabilities of the iron complexes of the parent acids (1:2 > 2:3 > 2:1). It thus appears that those factors which govern the stability of the iron complexes and the rates of hydrolysis (the ease of formation of the "transition state")[15,16] are operating in the same direction, but not to the same extent. In fact, a plot of the log K_3 (stability constants) against the log k_2 (specific rate constants of hydrolysis) gives a straight line relationship[15] (see Fig. 4). As postulated to explain the great difference in rates of hydrolysis between 2:1 and 1:2 acid phosphates, the relative instability of the iron complex of the 2:1 acid as compared to the 1:2 acid may be accounted for by supposing that the perihydrogen (8-position) hinders, sterically, in the former case, the necessary coplanarity that the carboxyl group must assume in the complex.

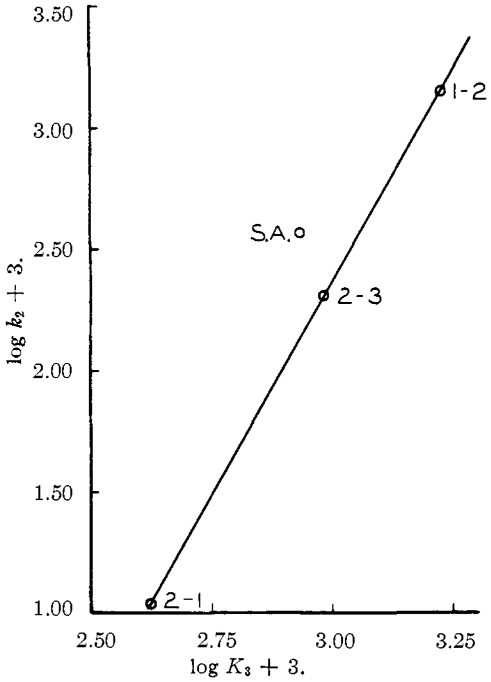

Fig. 4.—Log of the specific rate constant (k_2) for the hydrolysis of the phosphate ester against the log of the stability constant (K_3) of the Fe(III) complex of the parent acid. 1:2, 2:3, 2:1, and S.A. are 1-hydroxy-2-naphthoic, 2-hydroxy-3-naphthoic, 2-hydroxy-1-naphthoic and salicylic acids, respectively.

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New York, N. Y.

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