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Metal(III)-Salicylate Complexes: Protonated Species and Rate-Controlling Formation Steps

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In a recent study of the reaction of salicylate with iron(III), Dash and Harris[1] have suggested that a protonated iron(III)–salicylate complex is required to explain the kinetic data. Such protonated species have been proposed previously for salicylate complexes with vanadium(III),[2] gallium(III),[3] chromium(III),[4] and nickel(II).[5] However, another recent study[6] of the reaction of several salicylate derivatives with iron(III) did not invoke protonated complexes. Unfortunately, the analysis of Dash and Harris[1] appears internally inconsistent, and the conclusions might be considered suspect. Dash and Harris treated the formation and dissociation reactions as independent processes and analyzed the formation data as if first-bond formation was rate determining, while suggesting that "chelate-ring opening appears to be rate determining" for the dissociation reaction. But microscopic reversibility does not allow different rate-controlling steps in the forward and reverse reactions under the same conditions.

The purpose of the present note is to give a consistent analysis of the excellent and extensive data of Dash and Harris and to provide some coherent relationship between the various studies on iron(III)–salicylate systems. In addition, the question of whether first-bond formation or chelate-ring closing is the rate-controlling step for these systems is considered.

The formation and dissociation data of Dash and Harris[1] should be analyzed together to determine the full rate law and show that there is no inconsistency. The kinetic scheme of Dash and Harris can be modified as follows to retain the relationship between the forward and reverse reactions and the overall equilibrium constant (Scheme I). In Scheme I,

Scheme I

$$\mathrm{FeOH_2^{3+} \rightleftharpoons FeOH^{2+} + H^+} \qquad K_m$$

$$\mathrm{H_2Sal \rightleftharpoons HSal^- + H^+} \qquad K_a$$

$$\mathrm{FeOH_2^{3+} + HSal^- \rightleftharpoons FeHSal^{2+}} \qquad k_1, k_{-1}$$

$$\mathrm{FeOH^{2+} + HSal^- \rightleftharpoons FeSal^+ + H_2O} \qquad k_2, k_{-2}$$

$$\mathrm{FeOH^{2+} + H_2Sal \rightleftharpoons FeHSal^{2+} + H^+} \qquad k_3, k_{-3}$$

$$\mathrm{FeOH_2^{3+} + H_2Sal \rightleftharpoons FeHSal^{2+} + H^+} \qquad k_4, k_{-4}$$

$$\mathrm{FeHSal^{2+} \rightleftharpoons FeSal^+ + H^+} \qquad K_a''$$

k_i and k_{-i} are rate constants for the forward and reverse reactions, respectively, and all equilibrium constants are acid dissociation constants. After some manipulation, Scheme I predicts that the observed pseudo-first-order rate constant is given by

$$k_{obsd} = [k_2K_mK_a + (k_1K_a + k_3K_m)[\mathrm{H^+}] + k_4[\mathrm{H^+}]^2] \times \left[\frac{[\mathrm{Fe^{3+}}]_{tot}}{(K_m + [\mathrm{H^+}])(K_a + [\mathrm{H^+}])} + \frac{K_a''}{K_fK_a(K_a'' + [\mathrm{H^+}])}\right] \quad (1)$$

where $K_f = [\mathrm{FeSal^+}][\mathrm{H^+}]/[\mathrm{FeOH_2^{3+}}][\mathrm{HSal^-}]$. If salicylate is the reagent in excess, $[\mathrm{Fe^{3+}}]_{tot}$ is replaced by total salicylate concentration.

Table I. Reanalysis Results for the Formation and Dissociation of Iron(III) Salicylate[a,b] (1 M $NaClO_4$-$HClO_4$)

t, °C	K_a'', M	$k_1K_a + k_3K_m$, s^{-1}	$10^2k_2K_mK_a$, s^{-1}	$10^{-2}K_f$
20	0.82 ± 0.10	3.12 ± 0.18	2.50 ± 0.29	3.92 ± 0.31
	1.29 ± 0.16	3.78 ± 0.11	1.79 ± 0.29	5.40[d]
	0.53[c]	3.46[c]	2.97[c]	5.40[c]
25	0.79 ± 0.04	5.82 ± 0.13	4.04 ± 0.20	4.56 ± 0.14
	0.96 ± 0.05	6.42 ± 0.09	3.47 ± 0.23	5.40[d]
	0.61[c]	5.71[c]	4.85[c]	5.40[c]
30	0.88 ± 0.06	9.69 ± 0.26	8.77 ± 0.43	5.40 ± 0.2
	0.88 ± 0.04	9.69 ± 0.13	8.77 ± 0.38	5.40[d]
	0.76[c]	8.94[c]	11.6[c]	5.40[c]

[a] The data of Dash and Harris[1] have been analyzed by using the procedure and K_m values in footnote 14 of their work. [b] Errors represent one standard deviation. [c] Parameters given by Dash and Harris.[1] [d] The K_f was held fixed at this value during the least-squares analysis.

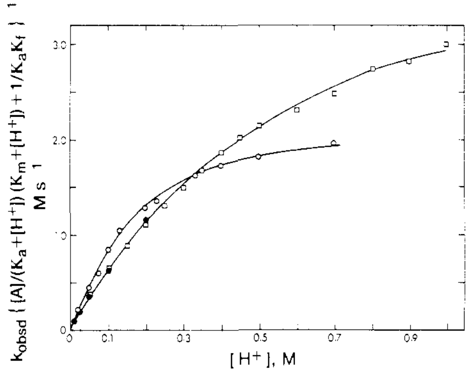
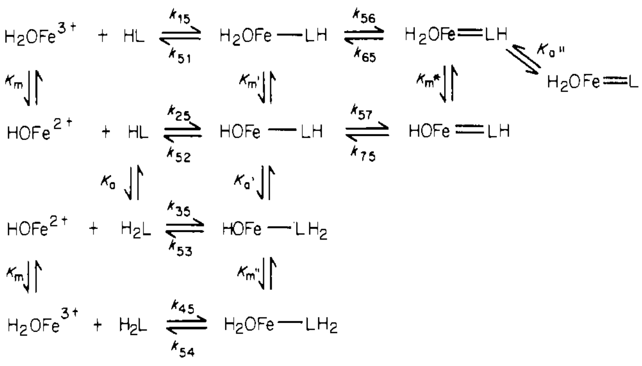


Figure 1. Plot of k_{obsd} $[([\mathrm{A}]/(K_a + [\mathrm{H^+}])(K_m + [\mathrm{H^+}]) + 1/K_aK_f)]^{-1}$ against $[\mathrm{H^+}]$ for the formation (●) and dissociation (□) of iron(III) salicylate using representative data from ref 1 (25 °C, μ = 1.0, [A] ≡ total iron(III)) and for iron(III) hydroxyphenylacetate (○) data from ref 12 (25 °C, μ = 1.0, [A] ≡ total ligand). Plots whould be linear if $K_a'' >> [\mathrm{H^+}]$. Lines drawn are calculated from the least-squares fit with K_a' = 0.82 M for salicylate and K_a'' = 0.28 M for hydroxyphenylacetate.

Scheme II



The results of a nonlinear least-squares fit to eq 1 of the combined formation and dissociation data of Dash and Harris are summarized in Table I. The two data sets are consistent with one set of parameters, although these are somewhat different from the values of Dash and Harris. The value of k_4 was undefined in the preliminary analysis and was omitted from subsequent fits. The data do require the protonated species $\mathrm{FeHSal^{2+}}$ with an acid dissociation constant $K_a'' \approx 0.8$ M. This can be seen from Figure 1 where the plot should be linear, or curving upward at high $[\mathrm{H^+}]$ due to $k_4[\mathrm{H^+}]^2$, if $K_a'' >> [\mathrm{H^+}]$.

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(1) Dash, A. C.; Harris, G. M. *Inorg. Chem.* **1982**, *21*, 2336.
(2) Perlmutter-Hayman, B.; Tapuhi, E. *J. Coord. Chem.* **1979**, *9*, 177.
(3) Corigli, R.; Secco, F.; Venturini, M. *Inorg. Chem.* **1982**, **21**, 2992.
(4) Liang, A.; Gould, E. S. *J. Am. Chem. Soc.* **1970**, *92*, 6791. In ref 15, the authors note the chromium(III) complex is half-protonated in 0.4 M $HClO_4$.
(5) Chopra, S., Jordan, R. B. *Inorg. Chem.* **1983**, *23*, 1708.
(6) Mentasti, E.; Secco, F.; Venturini, M. *Inorg. Chem.* **1982**, *21*, 602.

0020-1669/83/1322-4160$01.50/0

In view of the large number of kinetic studies on iron(III) salicylates, it seems unusual that the K_a'' effect was not observed previously. Dash and Harris have noted that the nitrate complexing[7] probably complicates the early studies of Saini and Mentasti.[8] For ligands such as 5-chlorosalicylate, 5-sulfosalicylate, and 5-nitrosalicylate, the phenol K_a is 10–1000 times larger than for salicylate and K_a'' should be larger as well. Therefore the kinetic effect of K_a'' would be detectable only at much higher than normal acidities for these systems. It is apparent from Figure 1 that if $[H^+]$ is only studied to <0.4 M, the k_a'' effect will be difficult to detect. This explains the results for 6-hydroxysalicylate[6,9] and some α-hydroxy carboxylates,[10] for example.[11]

The above explanations do not apply to the study of the iron(III)–hydroxyphenylacetate (mandelate) system by Cavasino et al.[12] The aliphatic OH proton should not be more acidic than the phenolic salicylate proton, and acidities up to 0.70 M were studied. An unusual acid dependence was noted[12] for this system, and it was attributed to a slow proton-transfer step. However, as can be seen in Figure 1, the hydroxyphenylacetate reaction is qualitatively similar to that of the salicylate system. A least-squares fit[13] of the stopped-flow data of Cavasino et al.[12] to eq 1 gives $K_a'' = 0.28 \pm 0.04$; $k_1K_a + k_3K_m = 9.3 \pm 0.6\ s^{-1}$ and $k_2K_{mKa} = (1.5 \pm 1.8) \times 10^{-2}\ s^{-1}$. Clearly the latter value is not defined by the data, but K_a'' is well-defined and of the expected magnitude.

A survey of other M^{3+}–salicylate systems indicates that $MHSal^{2+}$ complexes have been identified with vanadium(III) ($K_a'' = 0.11$ M, 27 °C, $\mu = 1.0$)[2], gallium(III) ($K_a'' = 0.057$ M, 25 °C, $\mu = 0.2$),[3] and chromium(III) ($K_a'' = 0.4$ M).[4] The gallium(III)–5-chlorosalicylate and –5-nitrosalicylate systems have K_a'' values of 0.11 and 0.29 M, respectively (25 °C, $\mu = 0.2$).[3] The variation of K_a'' with the K_a of the ligand phenol proton is in the expected direction and consistent with the arguments above for the failure to detect K_a'' for substituted salicylates reacting with iron(III).

The analysis outlined above is typical of that used to date. It is widely assumed that the values of k_1, k_2, k_3, and k_4 extracted from the analysis are specific rate constants for first-bond formation. The common rationale for this is that chelation will be faster than first-bond formation, because it is a unimolecular process (for a recent example see Ishihara et al.[14]). In fact, the important factor is the rate of chelate formation relative to the rate of dissociation of the monodentate species. Analysis in terms such as Scheme I simply indicates the metal ion ligand and proton composition of the transition state and gives no indication of the rate-controlling step.

To assess which step is rate limiting, a more detailed system such as Scheme II must be used. In this scheme the equilibrium constants (K) are all written as acid dissociation constants and are assumed to represent rapidly established equilibria. The ligand charges have been omitted for the sake of generality, but the ligand is assumed to be a dibasic acid (H_2L), analogous to salicylic acid in that the ionization of the second proton is omitted because $[H^+]$ is much larger than the second ionization constant. First-bond formation is assumed to be at the carboxylate function for charge and steric reasons. The intermediate species ($H_2OFe{-}LH$, $H_2OFe{-}LH_2$, etc.) are monodentate complexes, while the products ($H_2OFe{=}LH$, etc.) are bidentate complexes. If a steady state is assumed for the intermediates, then it can be shown that the observed pseudo-first-order rate constant is given by

$$k_{obsd} = \frac{f_{AB}}{\dfrac{k_{51}}{k_{15}K_a}\left(\dfrac{f_{AB}}{k_{56}[H^+] + k_{57}K_m'}\right) + 1} \times \left[\frac{[A]}{(K_a + [H^+])(K_m + [H^+])} + \frac{K_a''}{K_fK_a(K_m^* + K_a'' + [H^+])}\right] \quad (2)$$

where $f_{AB} = k_{25}K_mK_a + (k_{15}K_a + k_{35}K_m)[H^+] + k_{45}[H^+]^2$, $K_f = [FeL][H^+]/[FeOH_2][HL]$, and [A] is the total concentration of the reagent in excess under pseudo-first-order conditions.

As expected, this rate law has two limiting forms that depend on the magnitude of $k_{51}f_{AB}/k_{15}K_a$ relative to $(k_{56}[H^+] + k_{57}K_m')$. If the former term is larger, then chelate-ring closing is rate limiting, while if the latter term is larger, first-bond formation is rate limiting. Estimates of these terms, based on the water-exchange rate on iron(III),[15] the kinetics and formation constants of the iron(III)–monochloracetate[16] and –phenol[17] systems, and the hydrolysis constant of $(H_2O)_5FeCl^{2+}$[18] indicate a clear decision as to the dominant term cannot be made wtihin the uncertainties of the estimates.[19]

It can be seen from eq 2 that it may be difficult to determine the correct limiting form because $f_{AB}/(k_{56}[H^+] + k_{57}K_m')$ may be a slowly varying function of $[H^+]$. Therefore the dependence of k_{obsd} will be dominated by f_{AB} in the numerator of eq 2. However, the rate constants derived by the conventional analysis will always be smaller than the true values of k_{25}, $k_{15}K_a + k_{35}K_m$, and k_{45} because the denominator of the first term in eq 2 is always >1.

This type of analysis should be extendable from iron(III) to gallium(III) salicylates[3] because K_m and the water-exchange rates are of similar magnitude. The main difference is in the formation constant values, which are much smaller for gallium(III). If data for salicylic acid are used, then $K_f/K_a'' = (k_{15}/k_{51})(k_{56}/k_{65})$ is 6–7 times smaller for gallium(III) than for iron(III). If the difference is due to a smaller k_{15}/k_{51} for gallium(III), then the denominator of the first term in eq 2 will be larger than for iron(III). This would account for the observation that the calculated values[3] assigned to k_{25} and $k_{35}K_m + K_{15}K_a$ for gallium(III) are smaller than expected for a dissociative mechanism. It seems reasonable to expect the dissociative ion-pair mechanism to be a lower limit for the reaction rate, and associative paths should cause rate enhancement over the dissociative path.

Registry No. H_2Sal, 69-72-7; Fe, 7439-89-6; Ga, 7440-55-3; mandelic acid, 90-64-2.

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(7) The formation constant of $FeNO_3^{2+}$ predicts about 30% of the iron(III) will be in this form in 1 M NO_3^-: Martell, A. E.; Smith, R. M. "Critical Stability Constants"; Plenum Press: New York, 1977; Vol. 4, p 50.

(8) Saini, G.; Mentasti, E. *Inorg. Chim. Acta* **1970**, *4*, 21, 585.

(9) A reanalysis of the published data[6] for this system shows that the results are not inconsistent with $K_a'' \approx 0.8$–0.9 M and $k_1K_a + k_3K_m = 31\ s^{-1}$; $k_2K_mK_a = 1.1\ s^{-1}$. The former value differs significantly from the published value[6] of 20 s^{-1}, which is not consistent with the data.

(10) Mentasti, E. *Inorg. Chem.* **1979**, *18*, 1512.

(11) This also explains the failure to observe K_a'' in the aluminum(III)–salicylate system that was studied to $[H^+] = 0.20$ M: Secco, F.; Venturini, M. *Inorg. Chem.* **1975**, *14*, 1978.

(12) Cavasino, F. P.; Di Dio, E.; Skrizilo, C. *J. Chem. Soc., Dalton Trans.* **1981**, 2414.

(13) It was assumed that $k_4 = 0$, $K_a = 6.76 \times 10^{-4}$ M, and $K_f = 2.20 \times 10^2$ and $K_m = 1.63 \times 10^{-3}$ M as in the original work.[11] Values of k_{obsd} were calculated from the k_f values given by using eq 2 of ref 12 at or in the middle of the range of ligand concentrations given.

(14) Ishihara, K.; Funahashi, S.; Tanaka, M. *Inorg. Chem.* **1983**, *22*, 194.

(15) Grant, M.; Jordan, R. B. *Inorg. Chem.* **1981**, *2*, 55.

(16) Perlmutter-Hayman, B.; Tapuhi, E. *J. Coord. Chem.* **1976**, *6*, 31.

(17) Cavasino, F. P.; Di Dio, E. *J. Chem. Soc. A* **1970**, 1151.

(18) Bryne, R. H.; Kester, D. R. *J. Solution Chem.* **1981**, *10*, 51.

(19) The estimated values are as follows: k_{15}, $1 \times 10^3\ M^{-1}\ s^{-1}$; k_{25}, $4 \times 10^4\ M^{-1}\ s^{-1}$; k_{35}, $2 \times 10^3\ M^{-1}\ s^{-1}$; k_{56}, $1.5 \times 10^2\ s^{-1}$; k_{57}, $1 \times 10^5\ s^{-1}$; k_{15}/k_{51}, 125 M^{-1}; K_a, 1.6×10^{-3} M; K_m, 1.6×10^{-3} M; K_m', 6×10^{-5} M.