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Mechanism of Reaction of Iron(III) with Phenolic Derivatives

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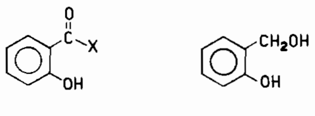
The complex formation reactions between iron(III) and four phenolic derivatives, salicylamide (A), salicylaldehyde (B), 2-hydroxyacetophenone (C) and 2-(hydroxymethyl)phenol (D), have been investigated using the stopped flow technique. For the ligands (A), (B), (C), the mechanism involves the reaction of the protonated ligands with both Fe^{3+} and $FeOH^{2+}$ (second order rate constants at $T = 25$ °C, $I = 1.0$M ($LiClO_4$) are Fe^{3+} + (A), (B), (C) 14.5, 2.6, and 3.0 M^{-1} s^{-1} respectively and $FeOH^{2+}$ + (A), (B), (C) 2900, 1370, and 1840 M^{-1} s^{-1}). For (D), only the reaction of $FeOH^{2+}$ with the ligand is observed ($FeOH^{2+}$ + (D) 1000 M^{-1} s^{-1}). Thermodynamic parameters have been evaluated and the data are compared with other systems of this type. The complexation mechanism is considered to involve some degree of associative character.

Introduction

The kinetics and mechanisms of complex formation reactions of iron(III) in aqueous acidic media have been studied extensively [1–4]. There are, however, relatively few data pertaining to the hexa-aquo ion, $Fe(H_2O)_6^{3+}$, owing to the greater reactivity of the first hydrolysis product $(H_2O)_5FeOH^{2+}$. In the light of recent evidence on the associative–dissociative character of trivalent ions [5–7], more information on the hexa-aquo ion is desirable. A second area of interest is an extension of studies to include ligands of high basicity such as phenolic derivatives. Previous attempts to evaluate rate parameters for the reactions between $Fe(H_2O)_6^{3+}$ and these basic monodentate ligands have been unsuccessful [8–10] in all cases except for phenol itself [4]. Instead the reaction pathway involves the $FeOH^{2+}$ ion and this has led to the proposal [9] that these reactions involve initial proton transfer from the phenolic residue to the hydroxy-metal ion in an outer-sphere complex followed by inner-sphere–outer-sphere interchange characteristic of the hexa-aquo ion.

In this study, the reactions of iron(III) with salicylaldehyde, salicylamide, 2-hydroxyacetophenone and 2-hydroxymethylphenol have been examined. These phenolic derivatives have differing functional groups adjacent to the hydroxy residue



X = H, NH_2,Me,(OH)

and are capable of forming chelate complexes as is apparent from their enhanced thermodynamic stabilities [11] over monodentate phenols of comparable basicity. Previous studies of the reactions of iron(III) with salicylaldehyde [12] and the related salicylic acid [13] have been reported and in both these systems complex formation pathways *via* $Fe(H_2O)_6^{3+}$ and $FeOH^{2+}$ have been identified.

The mechanistic interpretation is complicated by the possibility of chelate ring closure playing a role in the determining step. It has been found, however, with a great number of ligands [14–16] that the replacement of the first co-ordinated water molecule is generally slower than the subsequent substitution of the remaining donor atoms on the ligand. Such is the situation obtaining in the reactions of *o*-aminophenol where a single relaxation signal is observed [4]. Comparison is also possible with the relevant data for phenol which are also available.

Experimental

Stock solutions of iron(III) perchlorate, sodium perchlorate and perchloric acid were prepared and determined as described previously [17]. Lithium perchlorate was prepared by the slow addition of Li_2CO_3 (Hoptkin and Williams) to $HClO_4$ solutions at 70 °C. After recrystallization (three times) from

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TABLE I. Absorption Maxima, Molar Extinction Coefficients, and Equilibrium Constants for Complexes between Iron(III) and Phenolic Substrates, I = 1.0*M*.

Ligand	λ_{max} (nm)	ϵ_{max} (M^{-1} cm^{-1})	K_1	T °C	K_a[a]
Salicylamide	525	1500[a]	13.9 ± 2	15.4	
			15.1 ± 1	20.4	
			15.1 ± 1	25.0	1.25×10^{-9}
			16.5 ± 2	35.3	
2-Hydroxyacetophenone	530	1300[a]	0.49 ± 0.1	10.0	
			0.55 ± 0.1	15.0	
			0.65 ± 0.1	20.0	
			0.75 ± 0.1	25.0	1.58×10^{-11}
Salicylaldehyde	550	1200[a]	0.92 ± 0.02	12.3	
			1.13 ± 0.03	25.0	1.6×10^{-9}
Salicylic acid[b]	530	1620	7.4	25.0	
2-(Hydroxymethyl)phenol	560	2000 ± 500[c]	0.03	10.0	
			0.03	15.0	
			0.042	20.0	
			0.045	25.0	
Phenol[b]	556	1950	0.017	25.0	

[a] Ref. 11. [b] Z. L. Ernst and F. G. Herring, *Trans. Farad. Soc.*, *59*, 2838 (1963); *61*, 454 (1965). [c] See text.

water a stock solution was standardized by hydrogen ion exchange methods and titration against 0.1*M* NaOH.

Salicylaldehyde (Hopkin & Williams) and 2-hydroxyacetophenone (Koch-Light) were re-distilled under vacuum. 2-(hydroxymethyl)phenol (Koch-Light) was twice recrystallized from ether to yield white platelets. Salicylamide (B.D.H.) was recrystallized from ethanol. In all cases elemental analyses and melting points indicated a purity greater than 99.7%. Stock solutions were prepared daily by dissolving appropriate samples in the required amounts of $HClO_4/ClO_4^-$ solutions. Kinetic measurements were made using a stopped-flow spectrophotometer employing procedures described earlier [18]. Temperature control within the flow system was to better than ±0.1 °C. Solutions were prepared using 1.0*M* $LiClO_4$ as a background electrolyte. Several experiments were repeated with $NaClO_4$ and no significant medium effects were noted. Reactions were monitored at the wavelength maxima of the various complexes shown in Table I. Pseudo first order conditions were maintained with an excess of metal ion to avoid complications arising from formation of bis-complexes and first-order kinetic behaviour to greater than 90% reaction was normally observed.

Results and Discussion

In the conditions of acidity used in this study, ($[H^+] > 0.20M$) the major reactant species in solution are $Fe(H_2O)_6^{3+}$ and the protonated forms of the ligand HL. Optimum conditions for the formation of 1:1 complexes were achieved using an excess of metal ion and overall equilibrium absorbance measurements are consistent with equation (1)

$$Fe^{3+} + HL \rightleftharpoons FeL^{2+} + H^+ \quad (K_1) \qquad (1)$$

in which a single proton is released on complex formation (water molecules have been omitted for convenience). Final absorbance values A_∞ were found to be directly proportional to $[Fe(III)]_{total}$, and measurements of the graphical type used by Benesi and Hildebrand [19] were thus unsuitable for the evaluation of K_1. Using the extinction coefficients of Agren [11], however, equilibrium constants were evaluated from a knowledge of $[FeL^{2+}]$ ($= A_\infty/\epsilon l$) where l = 0.5 cm. In the case of the hydroxymethylphenol $\epsilon = 2 \pm 0.5 \times 10^3$ M^{-1} cm^{-1} was estimated from the data and from a consideration of values for similar phenolic ligands. Data for extinction coefficients and equilibrium constants are shown in Table I. Although trends in K_1 with temperature are discernible the spread of values is small and (ΔH_f° consequently has a low value. Since ΔG° is approximately zero so also is ΔS_f°. The K_1 values are in good agreement with those reported previously [11] at conditions of higher ionic strength. Of interest is the higher stability constant of salicylamide compared to the other substrates even though it has a basicity comparable to salicylaldehyde. This has been attributed [20] to greater resonance stabilization of the chelate ring.

TABLE II. Kinetic, Spectrophotometric and Equilibrium Data for the Reactions with Iron(III), T = 25.0 °C, I = 1.0*M* $LiClO_4$.

$[H^+]/M$	$10^3[Fe(III)]/M$	$10^3[A]$	k_{obs}/s^{-1}	10^2A_∞[a]
2-Hydroxyacetophenone (C)[c]				
0.300	14.58	2.40	5.02	2.38
	29.17		5.00	4.63
	43.75		5.23	6.88
	58.33		5.42	8.65
0.400	12.50	2.96	4.90	1.92
	25.00		5.17	3.80
	37.50		5.21	5.40
	50.00		5.38	7.15
Salicylamide (A)				
0.250	6.864	0.881	0.528	
	11.44		0.642	
	16.02		0.752	
	22.88		0.901	
0.350	6.864	1.065	0.503	15.20
	11.44		0.584	22.0
	16.02		0.686	28.0
	22.8		0.808	33.5
0.400	5.49	1.426[b]	0.529	15.1
	7.32		0.572	19.0
	10.98		0.611	26.8
	18.30		0.710	37.2
	21.96		0.774	41.7
0.550	6.864	1.175	0.568	10.8
	11.44		0.617	17.0
	16.02		0.662	23.2
	22.88		0.772	28.5
	5.49	1.234[b]	0.577	9.35
	7.32		0.532	12.0
	10.98		0.606	16.6
	14.64		0.691	20.8
	18.30		0.711	24.6
	21.96		0.768	26.9
Salicylaldehyde (B)				
0.300	2.821	2.828	2.76	1.91
	4.937		2.83	3.36
	7.053		2.80	4.91
	8.463		2.79	5.75
	14.11		2.87	9.96
0.350	4.94	2.970	2.85	2.66
	11.28		2.96	5.87
	14.11		2.93	6.87
0.400	9.152	6.234	3.08	9.80
	18.30		3.19	19.60
	27.46		3.18	29.60
	45.76		3.31	47.5
0.500	6.86	4.934	3.24	4.33
	9.15		3.22	5.74
	11.44		3.22	7.24
0.600	4.576	4.934	3.39	4.94
	13.73		3.45	7.04
	22.88		3.53	12.1
2-(hydroxymethly)phenol (D)[c]				
0.30	29.17	6.14	35.2	1.72
	43.75		36.7	1.20
	58.33		36.5	2.27
0.40	25.0	5.90	33.7	0.68
	37.5		36.7	0.91
	50.0		39.3	1.35
0.50	31.25	6.04	33.8	0.67
	41.67		36.5	0.87
0.60	33.33	6.01	37.0	0.64

[a] Absorbance of reactant solution at equilibrium, optical pathlength 0.50 cm. [b] $NaClO_4$ as supporting electrolyte. [c] Optical pathlength 0.20 cm.

By analogy with reactions of other substrates with iron(III), equilibrium (1) may be attained by four possible pathways (2)–(5):

$$Fe^{3+} + HL \underset{k_1}{\overset{k_1}{\rightleftharpoons}} FeL^{2+} + H^+ \qquad (2)$$

$$H^+ + Fe^{3+} + L^- \underset{k_4}{\overset{k_3}{\rightleftharpoons}} FeL^{2+} + H^+ \qquad (3)$$

$$H^+ + FeOH^{2+} + HL \underset{k_6}{\overset{k_5}{\rightleftharpoons}} FeL^{2+} + H^+ \qquad (4)$$

$$2H^+ + FeOH^{2+} + L^- \underset{k_8}{\overset{k_7}{\rightleftharpoons}} FeL^{2+} + H^+ \qquad (5)$$

It should be noted that as written these are composite reactions possibly involving a chelation process. If the initial replacement of the coordinated water molecule of the metal ion is rate controlling, however, *i.e.* ring closure is fast, then the observed forward rate constant k_1 *etc.* represents the overall rate of chelate formation. This situation has been shown to obtain in the majority of the reactions of iron(III) studied to data. Taking into account the protonation equilibria

$$Fe^{3+} \rightleftharpoons FeOH^{2+} + H^+ \quad K_h \qquad (6)$$

and

$$HL \rightleftharpoons H^+ + L^- \quad K_a \qquad (7)$$

since Fe^{3+} is the major iron(III) species present in solution [21] and the conditions of constant $[H^+]$ prevail ($[H^+] > 0.2M$) the rate expression (8) may be derived

$$d[FeL^{2+}]/dt = \{k_\alpha[Fe^{3+}]_{tot} + k_\beta\} \qquad ([FeL^{2+}]_\infty - [FeL^{2+}]_t \qquad (8)$$

where

TABLE III. Formation Rate Constants for the Reactions.

Ligand	T °C		$k_1{}^a$	$10^{-3}\ k_s^a$
Salicylamide	15.4		6 ± 1	2.1 ± 0.3
	20.4		9 ± 1	3.2 ± 0.3
	25.0		14.5 ± 1	2.9 ± 0.3
	35.3		40 ± 10	5.0 ± 0.5
		$\Delta H^{\ddagger b}$	17.3 ± 2	7.5 ± 2
		$\Delta S^{\ddagger c}$	6 ± 4	−19 ± 4
Salicylaldehyde	12.3		0.5 ± 0.1	0.76 ± 0.05
	25.0		2.6 ± 0.3	1.37 ± 0.08
		$(\Delta H^{\ddagger b}$	22.1 ± 5	7.5 ± 3)
		$(\Delta S^{\ddagger c}$	11 ± 4	−18 ± 4)
2-Hydroxyacetophenone	10.0		0.42 ± 0.1	0.64 ± 0.2
	15.0		0.72 ± 0.2	0.79 ± 0.3
	20.0		1.63 ± 0.4	1.33 ± 0.4
	25.0		3.04 ± 0.5	1.84 ± 0.5
		$\Delta H^{\ddagger b}$	22.1 ± 3	11.8 ± 1.2
		$\Delta S^{\ddagger c}$	18 ± 4	−4 ± 4
2-(Hydroxymethyl)phenol	10.0			0.50 ± 0.3
	15.0			0.60 ± 0.3
	20.0			0.85 ± 0.4
	25.0			1.00 ± 0.4
		$\Delta H^{\ddagger b}$	–	7.32 ± 2
		$\Delta S^{\ddagger c}$	–	−20 ± 6
Salicylic Acid[d]	25.0		3.0	5.5
$\Delta H^{\ddagger b}$			–	12
$\Delta S^{\ddagger c}$			–	−2

[a] Units are $M^{-1}\ s^{-1}$. [b] Kcal/mol. [c] Cal/deg/mol. [d] Ref. 13.

TABLE IV. Rate Constants[a] for Reactions of Fe^{3+} and $FeOH^{2+}$.

Ligand	$k_1(M^{-1}\ s^{-1})$	$10^4 k_3(M^{-1}\ s^{-1})$
Salicylamide	14.5	0.29
Salicylaldehde	2.6	0.137
2-(Hydroxyacetophenone	3.0	0.18
Salicylic Acid	3.0	0.55
Phenol	25	0.072
o-Amino-phenol	–	11.0
2-(Hydroxymethyl)phenol	–	0.10
m-Nitrophenol	–	0.06
o-Hydroxyphenol[b]	–	0.31
Cl^{-c}	9.4	–
NCS^{-d}	127	–

[a] Data are at T = 25 °C, various ionic strengths. [b] Ref. 25. [c] R. E. Connick and C. P. Coppel, *J. Am. Chem. Soc.*, *81*, 6389 (1959). [d] H. Wendt and H. Strehlow, *Z. Elektrochem.*, *66*, 228 (1962).

$$k_\alpha = k_1 + k_3K_a/[H^+] + k_5K_h/[H^+] + k_7K_aK_h/[H^+]^2 \qquad (9)$$

and

$$k_\beta = \frac{1}{K_1}\{k_1[H^+] + k_3K_a + k_5K_h + k_7K_aK_h/[H^+]\} \qquad (10)$$

Plots of $k_{obs} = (k_\alpha[Fe(III)]_{tot} + k_\beta)$ against $[Fe(III)]_{tot}$ should be linear (equation 8). Only in the case of salicylamide where the equilibrium constant is sufficiently large were the slopes of such plots (k_α) great enough compared to experimental error to give values which could be plotted meaningfully against $[H^+]^{-1}$. In other cases, values of k_{obs} did not vary markedly with $[Fe(III)]_{tot}$. Representative data at 25 °C are presented in Table II and those at other temperatures may be found in thesis form elsewhere [21]. In all cases, however, the intercepts k_β when plotted against $[H^+]$ (Equation (10)) yielded straight lines with gradients k_1/K_1 and intercepts $\{k_3K_a + k_5K_h\}/K_1$. The slopes of these plots may thus be related unambiguously to the rate constant k_1 for the reaction of $Fe(H_2O)_6^{3+}$ with the protonated form of the ligand. The lack of any term in $[H^+]^{-1}$ in the hydrogen ion correlation of k_β is consistent with the absence of any reaction pathway (5) involving $FeOH^{2+}$ and L^-. This situation is similar to that in other reaction systems of this type where the rate constant would exceed that of the diffusion controlled limit. Using K_1 the rate parameters k_1 and $\{k_3K_a + k_5K_h\}$ were evaluated and as has been found for other systems, where ligands of high basicity are involved [4, 23], interpretation of the composite constant in terms solely of k_3K_a leads to a forward rate for (3) which is close to or exceeds the diffusion controlled limit. The constant is therefore considered to correspond principally to k_5K_h. Rate constants evaluated at various temperatures and related thermodynamic parameters are presented in Table III.

In the case of three of the four systems under investigation there is clear evidence in the mechanism for the Fe_{aq}^{3+} pathway as well as that involving the hydroxo complex. For the (2-hydroxymethyl)phenol, however, both initial rate data and overall reaction constants are consistent with only the $FeOH^{2+}$ ion reacting. In this way these derivatives may be compared to salicylic acid [13] and phenol [4] where both ions are reactive and to *o*-aminophenol [4] where again only $FeOH^{2+}$ contributes to reaction. As expected, in no case yet studied is there evidence for only the Fe_{aq}^{3+} as the reactant.

In the formation of a metal ion complex the initial step is considered to be an ion pairing,

$$M + L \rightleftharpoons M, L \qquad K_{os}$$

followed by the rate-determining loss of a water molecule from the complexed metal centre to give an inner sphere species. The magnitude of the overall rate constant $k = k_{ex} \cdot K_{os}$ depends on both the outer sphere association constant and the rate of water exchange k_{ex}. It is generally considered that factors involving K_{os} are charge and the effects of solvation on ligand L. Since all the substrates in the present study have a similar charge, the most important factor ought to be ligand solvation. In an I_d mechanism, k_{ex} does not change significantly with the same metal ion and ligands of similar structure. Differences in K_{os} should therefore appear as variations in the observed rate constants. For the hexa-aquo ion, the rates and thermodynamic parameters for the reactions with 2-hydroxyacetophenone and salicylaldehyde are comparable in magnitude to those for salicylic acid. The high rate constant for salicylamide cannot readily be explained by changes in outer-sphere association. Although a mechanism involving ring closure in the rate determining step cannot be ruled out (phenol[4] itself reacts with $k_{obs} = 25\ M^{-1}\ s^{-1}$) the trend in rate constants is consistent with the nucleophilic properties of the non-phenolic substituent and parallels the overall trend in complex stabilities. For the trivalent metal ions there is support for an I_a mechanism in which an element of bond making occurs within the outer-sphere complex. This is considered to be the case in the reactions of Mo(III) [24] and there is growing evidence that Co(III) may be the exception among M(III) species in undergoing anation by an I_d process [5]. The present data supplemented by those for other phenols are presented in Table IV where a slight spread of values for both the Fe_{aq}^{3+} and the $FeOH^{2+}$ pathways is discernible There is no obvious correlation of the rate constants with the basicity of the ligands and it may be that the associative interchange mechanism although operating is less well defined than for other ter-valent metal ions. The influence of ionic radius may be a factor and a study of pressure effects and activation volumes [5] on these systems could well provide additional information.

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