Kinetics of Formation of the
Monosalicylato Complex of Iron(III)

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The rate of formation of the monosalicylato complex of iron(III) has been investigated in acidic aqueous solution at 20.0°, 25.0° and 30.0°C and ionic strength 1.0 F (KNO₃). The complex formation has been studied by the stopped-flow technique over the range of acidity 0.600 ⩾ [H⁺] ⩾ 0.010. The experimental data have been compared with those obtained in a previous paper on the formation of monosulfosalicylato complex of iron(III). They give evidence that in the range of acidity investigated, the species of the ligand react essentially with FeOH²⁺, as suggested in the previous paper.

Introduction

In a previous paper,[1] the kinetics of formation of 1:1 ferric complex with sulfosalicylic acid (2-hydroxy, 5-sulfobenzoic acid) was investigated.

In order to elucidate the rôle of the basicity of ligand on the kinetics of reaction, it seemed of interest to investigate the kinetics of complex formation of salicylic acid with iron(III).

The molecules of the two ligands are very similar, but the basicity of their carboxylato groups is rather different, so that the comparison of kinetic data can be fruitful. Furthermore the negative charge of sulfosalicylato ligand is higher than that of salicylato, so that it is possible to investigate the effect of the charge of the ligand on the kinetics, owing to the fact that the charges of the reacting species can affect te equilibrium constant of the first step of the reaction, the formation of the outer sphere complex.

Salicylic acid, like sulfosalicylic acid, gives with Iron(III) a series of complexes such as $Fe(Sal)_n^{(2n-3)-}$ with n = 1, 2 and 3, with deprotonation both of carboxylic as well as phenol groups.[2,3,4]

Equilibrium data show that, by performing the reaction of the metal ion with the ligand in proper experimental conditions, it is possible to obtain FeSal⁺ without the higher complexes.[2]

To this purpose, the kinetic measurements were made in solutions with $[H^+] \geqslant 0.010$.

The concentrations of the reacting species were so chosen that the hydrogen ions displaced during the reaction did not modify appreciably the pH of the

solution and that the only hydroxylated complex existing in solution was $FeOH^{2+}$.

The kinetic measurements were made at 20.0°, 25.0° and 30.0°C in order to evaluate the activation parameters of the reaction.

The ionic strength 1.0 F was held constant by addition of KNO₃. Equilibrium data concerning the dissociation constant of salicylic acid and complex formation of FeSal⁺ in the experimental conditions investigated, were also determined.

Experimental Section

Materials. Iron(III) nitrate, salicylic acid, potassium nitrate, nitric acid and potassium hydroxide were reagent grade chemicals (C. Erba RP).

Standard solutions of nitric acid and potassium nitrate were used to bring the solutions to the proper acidity and ionic strength. In the range of experimental concentrations of H⁺, nitric acid was considered as fully dissociated, according to the literature data on its dissociation constant.[5,6]

The stock solution of iron(III) nitrate, acidified with nitric acid, was gravimetrically analysed for iron, while the content of free nitric acid was determined by alkali titration of the solution after exchange on a Dowex 50 W (H⁺ form) column, and correction for iron content of the solution.

The solutions of salicylic acid were prepared daily and protected from direct light.

Owing to the low solubility of the reagent, solutions of higher concentration of salicylic acid, were prepared by addition of potassium hydroxide. They were neutralized with nitric acid immediately before use.

Apparatus. The apparatus were the same described in the previous paper.[1]

Results and Discussion

Equilibrium constants. The dissociation constant K_A of the carboxylic group of salicylic acid was determined by pH-metric titrations with potassium hydroxide.

(1) G. Saini and E. Mentasti, *Inorg. Chim. Acta*, 4, 210 (1970).
(2) A. Ågren, *Acta Chem. Scand.*, 8, 1059 (1954).
(3) L. Vareille, *Bull. Soc. Chim. France*, 1493 (1955).
(4) P. Romain and J. C. Colleter, *Ibid.*, 867 (1958).

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(6) H. A. C. Mc Kay, *Trans. Faraday Soc.*, 52, 1568 (1956).

Table I. Equilibrium constants*

| Reaction	Constant	20.0°C	25.0°C	30.0°C	Reference
$Fe^{3+}+HSal^- \rightleftarrows FeSal^+ +H^+$	K_C	506 ± 6	532 ± 6	566 ± 6	This work
$Fe^{3+}+H_2O \rightleftarrows FeOH^{2+}+H^+$	K_{OH} (M)	1.23×10^{-3}	1.65×10^{-3}	2.19×10^{-3}	(8)
$H_2Sal \rightleftarrows HSal^- +H^+$	K_A (M)	$1.60\pm0.04\times10^{-3}$	$1.60\pm0.04\times10^{-3}$	$1.60\pm0.04\times10^{-3}$	This work
	ε_{FeSal^+}		$1470\pm30\ M^{-1}\,cm^{-1}$		This work

* Ionic strength = 1.0 F.

A plot of degrees of formation $\bar{g}$, *versus* pH, shows that the experimental data at 20.0°, 25.0° and 30.0°C lie on a single curve within experimental error (Figure 1), so that the value of K_A can be assumed as constant over the temperature range studied.
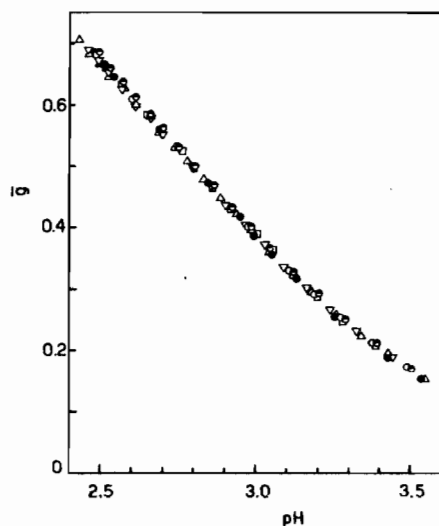
Figure 1. Plot of g, the degree of formation of salicylic acid, as a function of pH ($\mu = 1.0$ F).

△ $C_A = 12.2$ mM, 20.0°C;   ◐ $C_A = 10.0$ mM, 20.0°C;
▽ $C_A = 11.0$ mM, 25.0°C;   □ $C_A = 9.98$ mM, 25.0°C;
● $C_A = 12.2$ mM, 30.0°C;   ○ $C_A = 10.0$ mM, 30.0°C
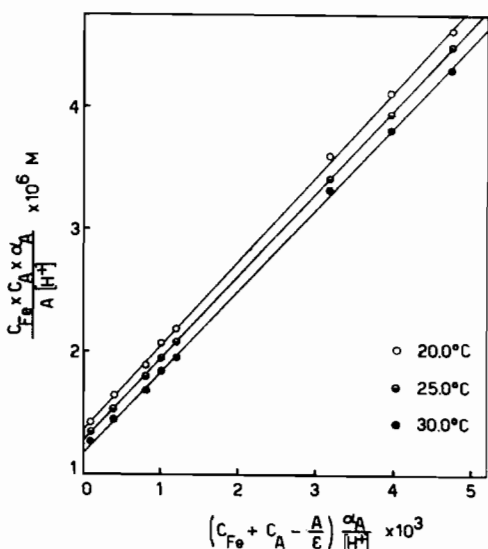
Figure 2. Plot of spectrophotometric data for evaluation of formation data of FeSal⁺, according to the method of Frank and Oswalt.[7]

The equlibrium constant K_C of FeSal⁺ formation, was determined spectrophotometrically at 530 nm by using the method of Frank and Oswalt[7] at $\mu = 1.0$ F (KNO₃) and $[H^+] = 0.100$ and 0.200. Figure 2 shows the plots of experimental data at the three temperatures investigated. α_A, the fraction of dissociated ligand, is equal to $K_A/(K_A+[H^+])$.

The value of K_{OH} at 25.0°C, the constant of formation of FeOH²⁺ by hydrolysis of Fe³⁺, was taken from a paper of Milburn,[8] whereas the values at 20.0° and 30.0°C were calculated from the ΔH of the reaction, given by the same author.

Table I collects the equilibrium data.

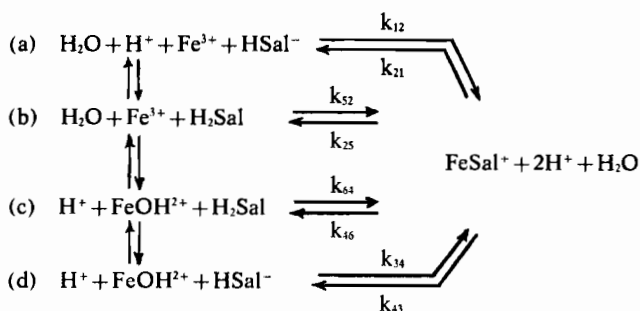**Table II.** Kinetic data for FeSal⁺ formation $\mu = 1.0$ F, $t = 25.0$°C

C_{Fe} mM	C_A mM	$[H^+]$ M	k_{obs} sec^{-1}	$(k_{obs}/B)\times10^{-3}$ M^{-1} sec^{-1}
30.0	0.75	0.600	7.3	6.0
25.0	0.75	0.600	7.4	6.2
20.0	0.75	0.600	7.2	6.1
30.0	0.75	0.500	6.6	6.4
25.5	0.75	0.500	6.8	6.7
20.0	0.75	0.500	6.3	6.3
15.0	0.75	0.500	6.3	6.4
30.0	0.50	0.300	4.7	6.7
25.0	0.50	0.300	4.3	6.4
20.0	0.50	0.300	4.1	6.4
15.0	0.50	0.300	4.0	6.5
30.0	0.30	0.200	3.8	6.2
25.0	0.30	0.200	3.6	6.3
20.0	0.30	0.200	3.5	6.5
15.0	0.30	0.200	3.1	6.3
30.0	0.30	0.100	4.0	6.1
25.0	0.30	0.100	3.5	6.0
20.0	0.30	0.100	3.2	6.4
15.0	0.30	0.100	2.6	6.1
10.0	0.30	0.100	2.1	6.1
0.30	8.0	0.030	2.7	6.1
0.30	7.5	0.030	2.7	6.5
0.30	6.5	0.030	2.4	6.5
0.30	6.0	0.030	2.3	6.7
0.30	8.0	0.020	3.8	6.5
0.30	7.5	0.020	3.9	7.1
0.30	7.0	0.020	3.6	7.0
0.30	6.5	0.020	3.1	6.4
0.30	8.0	0.015	5.3	7.3
0.30	7.5	0.015	5.0	7.4
0.30	7.0	0.015	4.8	7.5
0.30	6.5	0.015	4.6	7.8
0.30	6.0	0.015	3.9	7.1
0.30	8.0	0.010	7.9	8.2
0.30	7.5	0.010	7.5	8.3
0.30	7.0	0.010	6.8	8.0
0.30	6.5	0.010	6.2	7.9
0.30	6.0	0.010	5.8	8.0

(7) H. S. Frank and R. L. Oswalt. *J. Amer. Chem. Soc.*, 69, 1321 (1947).
(8) R. M. Milburn, *Ibid.*, 79, 537 (1957)

Table III. Average values of k_{obs}/B for $FeSal^+$ formation ($\mu = 1.0$ F); the range of C_{Fe} and C_A values for each acidity is the same as in Table II

$[H^+]$ M	$(k_{obs}/B) \times 10^{-3}$ $M^{-1} sec^{-1}$
	$t = 20.0°C$
0.500	3.8 ± 0.2
0.400	3.7 ± 0.2
0.300	3.8 ± 0.2
0.200	3.8 ± 0.3
0.100	3.6 ± 0.2
0.030	3.4 ± 0.2
0.020	3.6 ± 0.2
0.015	3.9 ± 0.3
0.010	4.0 ± 0.2
	$t = 30.0°C$
0.300	10.9 ± 0.4
0.200	10.9 ± 0.5
0.100	11.0 ± 0.4
0.030	11.7 ± 0.5
0.020	12.1 ± 0.4
0.015	12.9 ± 0.4
0.010	14.3 ± 0.6

Kinetics. The experimental data are given in Table II and III. The kinetic results are consistent with the following reaction scheme:

(a) $H_2O + H^+ + Fe^{3+} + HSal^- \underset{k_{21}}{\overset{k_{12}}{\rightleftarrows}}$

(b) $H_2O + Fe^{3+} + H_2Sal \underset{k_{25}}{\overset{k_{52}}{\rightleftarrows}}$

(c) $H^+ + FeOH^{2+} + H_2Sal \underset{k_{46}}{\overset{k_{64}}{\rightleftarrows}}$ $FeSal^+ + 2H^+ + H_2O$

(d) $H^+ + FeOH^{2+} + HSal^- \underset{k_{43}}{\overset{k_{34}}{\rightleftarrows}}$

By adopting the same assumptions given in the previous paper, the following expression can be obtained:

$$k_{obs} = (k_{12} + k_{64}K_{OH}/K_A + k_{52}[H^+]/K_A + k_{34}K_{OH}/[H^+])B \qquad (1)$$

where k_{obs} is the pseudo-first-order constant and the factor B is equal to $(C_{Fe}\alpha_A + [H^+]/K_C)$ for kinetic measurements at $[H^+] \geqslant 0.100$ (excess of metal), or $B = (C_A\alpha_A/(1 + K_{OH}/[H^+]) + [H^+]/K_C)$ (excess of ligand); so this factor takes into account the effect of acidity on equilibria of dissociation of salicylic acid, of hydrolysis of Fe^{3+}, and complex formation.

By plotting k_{obs}/B as a function of $[H^+]^{-1}$, the curves given in Figure 3 were found.

They allow us to evaluate the constant k_{34} corresponding to the term proportional to $[H^+]^{-1}$.

From experimental data, a constant independent of $[H^+]$, corresponding to the sum of the first two terms of (1): $k_o = k_{12} + k_{64}K_{OH}/K_A$, can also be calculated. Several arguments have been suggested to evaluate the contribution of the two terms to the value of k_o. In our previous paper we concluded that the main contribution in the case of the mono-sulfosalicylato complex of Fe^{III} came from the term $k_{64}K_{OH}/K_A$. By making the hypotesis that for the

two ligands investigated by us, the term k_{12} is negligible as compared with $k_{64}K_{OH}/K_A$ and under the assumption that k_{64} is independent of ligand, $(k_o)_{SS}/(k_o)_{Sal}$ must be equal to $(K_A)_{Sal}/(K_A)_{SS}$.
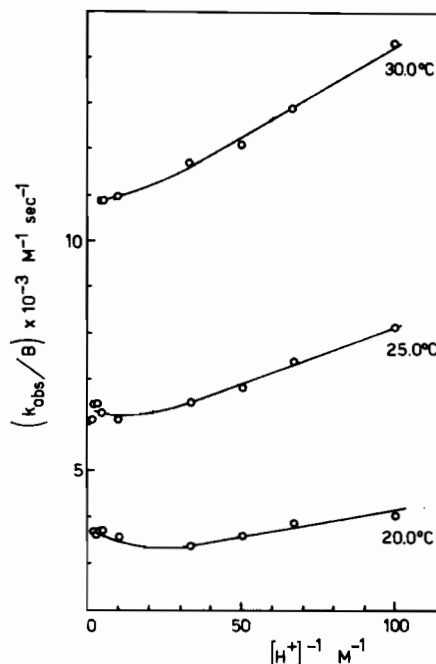
Figure 3. Dependence of k_{obs}/B as a function of $[H^+]^{-1}$, at the temperature values investigated.

Our experimental data at $25.0°C$ are in agreement with this hypothesis. This gives further support to our previous conclusion and indicates that reaction (a) of the above scheme does not give a significant contribution to the complex formation.

The present data suggest that useful information can be obtained by comparing the kinetic data concerning two ligands which differ only by the presence of one substitutent that does not take part in the complex formation, but greatly changes the basicity of the ligand.

The values of k_{34} and k_{64} were found to be:

	$20.0°C$	$25.0°C$	$30.0°C$
$k_{34}(M^{-1} sec^{-1})$	$8.8 \pm 0.8 \times 10^3$	$1.4 \pm 0.1 \times 10^4$	$1.7 \pm 0.1 \times 10^4$
$k_{64}(M^{-1} sec^{-1})$	$3.8 \pm 0.3 \times 10^3$	$5.5 \pm 0.5 \times 10^3$	$7.7 \pm 0.7 \times 10^3$

The nonlinear behaviour of the curves in Figure 3 shows the contribution of reaction (b) which becomes important in strongly acidic solutions. An evaluation of k_{52} cannot be made with good accuracy; in fact $Fe(H_2O)_6^{3+}$ reacts much more slowly than $Fe(H_2O)_5$-OH^{2+}, which takes part in reaction (c) and (d); furthermore with increasing acidity of the medium, the concentration of $FeSal^+$ at equilibrium decreases and consequently the variation of absorbance with time is very small.

The variation of the value of k_{52} with temperature, in the range investigated, was within the limits of experimental error.

Taking now into account the single steps of the complex formation, reactions (a) (b) (c) and (d) of

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the above scheme must also include the fast reactions of ion pair formation (outer sphere complex), so that the rate constants k_{52}, k_{64} and k_{34} must include the ion pair association constants K_i^*.

These constants have been often evaluated with the Fouss-Eigen relation,[9] which has been derived under the hypothesis of a ligand having a spherical form, and with the charge uniformly shared on it.

By considering that the values of K_i^* should increase with increasing charge of the ions which take part to the ion pair formation, the experimental rate constants should be higher for the monosulfosalicylato than for the monosalicylato complex.

Table IV. Rate constants $(M^{-1} \text{ sec}^{-1})$ for FeSS and FeSal$^+$ formation. $(\mu = 1.0 \text{ F}, \quad t = 25.0°)$

Complex	k_{52}	k_{34}	k_{64}
FeSS	1.5±1	1.2±0.1×10^4	5.5±0.5×10^3
FeSal$^+$	3.0±1	1.4±0.1×10^4	5.5±0.5×10^3

sulphonato group (which is in meta and para positions with carboxylic and phenolic groups respectively), seems not to be favourable to the complex formation.

Comparing now the values of the constants k_{52}, k_{64} and k_{34} with the rate constants of water exchange from the co-ordination sphere of $Fe(H_2O)_6^{3+}$ and $Fe(H_2O)_5OH^{2+}$ ions,[10] once again the rate determining step of the iron(III) complex formation appears to be essentially the release of water molecules from the inner co-ordination sphere of the metal ion.

Activation parameters. The results obtained from the measurements made in the limited range of temperatures (20.0°, 25.0° and 30.0°C), allowed an approximate estimate (within 30%) of the activation parameters to be made. They have been collected in Table V with others found in the literature, concerning iron(III) complexes formation.

The data show that activation enthalpies are in good agreement with the values found for other

Table V. Activation parameters for the formation of monocomplexes of Iron(III). (t = 25.0°C)

Reaction	μ F	ΔH_f^* kcal . mol^{-1}	ΔS_f^* cal.deg^{-1}. mol^{-1}	Reference
FeOH^{2+} + H$_2$Sal	1.0	12	−2	This work
FeOH^{2+} + HSal$^-$	1.0	11	−3	This work
FeOH^{2+} + HF	0.5	10	−8	12
FeOH^{2+} + CNS$^-$	0.4	10	−7.6	13
FeOH^{2+} + HN$_3$	0.1	9	−10	14
FeOH^{2+} + Cl$^-$	1.0	13	4	15
FeOH^{2+} + SO$_4^{2-}$	0.5	11.3	4	16
FeOH^{2+} + HSO$_4^-$	0.5	5	−18	17

The experimental data (see Table IV), do not support this expectation; this could be due first to the fact that the approximation of the spherical form seems to be unrealistic for this kind of ligand; moreover by considering that in the outer sphere complex, the metal ion must be in a favourable position for chelation, the electrostatic attraction of the

ligands, and bring support to the above conclusions.

The data concerning activation entropies are more scattered, and do not reveal a definite trend indicating a possible interpretation.

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