Contribution from the Istituto di Chimica Analitica
Università di Torino, Italy

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

G. Saini and E. Mentasti

Received December 23, 1969

The rate of formation of the monosulfosalicylic complex of iron(III) in aqueous solution has been studied by the use of a stopped-flow technique at 25.0°C and $\mu = 1.0$ M *(KNO_3). Measurements. made over an acidity range between* $[H^+] = 0.5$ M *and* 0.01 M, *suggest a mechanism which agrees with the available kinetic data on the formation of iron(III) complexes. The proposed mechanism confirms that the rate determining step is the water release from the inner co-ordination sphere of the metal ion.*

Introduction

Kinetic studies on the formation of Fe^{III} complexes in aqueous solution, have been recently directed to the behaviour of ligands of different basicity, with the aim to elucidate the reaction mechanism involved, both in the case of monodentate as well as bidentate ligands.[1-10]

Therefore it seemed of interest to perform the kinetic investigation of the reaction between Fe^{III} and sulfosalicylic acid (which will be later indicated with H_3SS).

This ligand in solution, at low pH values, is in the form H_2SS^-, owing to the high dissociation constant of sulphonic group; by further dissociation, it gives the weakly basic species HSS^{2-}.[11] By reaction with Fe^{III}, complexes such as $Fe(SS)_n$ (with $n = 1$, 2 and 3) are formed with displacement of hydrogen ions from the phenolic group.[11,12]

The dissociation constant of HSS^{2-} has been found to be of the order of 10^{-11} M,[13] and therefore, in acidic solutions, the concentration of SS^{3-} can be neglected.

The molar absorptivity of the complex FeSS is high at 500 nm,[11,12,14] and therefore its formation from the reagents can be followed photometrically with good accuracy.

Previous work on equilibria existing in the above solutions, has shown that no formation of protonated complexes occurs, and that in suitable experimental conditions, it is possible to obtain the complex FeSS without the formation of higher complexes.[11,12,14]

The present work has been performed at 25.0°C ±0.1 and $\mu = 1.0\,M(KNO_3)$. A series of kinetic measurements has been made in the presence of an excess of Fe^{III}. The $[H^+]$ was equal or higher than $0.1\,M$, and the concentration of Fe^{III} was such that the only hydroxy-complex of Fe^{III} present was $FeOH^{2+}$.

In a second series of measurements, an excess of ligand was used, and measurements were performed at various hydrogen ion concentrations higher than $0.01\,M$. In such conditions, the amount of hydrogen ions displaced by the reaction did not affect appreciably the pH of the solution under measurement and the only complex formed was FeSS.

The data available in the literature on equilibrium of the complex FeSS, and dissociation of H_2SS^-, concern ionic strengths different from that of the present work. Therefore equilibrium measurements at ionic strength $1.0(KNO_3)$ will be given.

Experimental Section

Materials. Iron(III) nitrate, potassium nitrate, nitric acid, potassium hydroxide and NaH_2SS were reagent grade chemicals (C. Erba RP). All reagents, with the exception of NaH_2SS which was recrystallized from water, were used without further purification.

The concentration of the iron(III) nitrate stock solution, was determined gravimetrically. KNO_3 was used to bring at constant ionic strength the solutions.

Apparatus. pH measurements were performed with a Beckman Research pH meter. An Hitachi Spectrophotometer mod. EPS-3T, equipped with 1.000 cm cells, was used to obtain spectrophotometric data concerning equilibrium determinations. Kinetic measurements were made with a Durrum-Gibson stopped-flow spectrophotometer at 500 nm. The procedure was the following: equal volumes of the solutions of Fe^{III} and of the ligand were mixed in the

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(1) J. F. Below Jr., R. E. Connick, and C. P. Coppell, *J. Am. Chem. Soc.*, *80*, 2961 (1958).
(2) R. E. Connick and C. P. Coppell, *J. Am. Chem. Soc.*, *81*, 6389 (1959).
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(5) G. G. Davis and W. MacF. Smith, *Can. J. Chem.*, *40*, 1836 (1962).
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(9) F. Accascina, F. P. Cavasino, and S. D'Alessandro, *J. Phys. Chem.*, *71*, 2474 (1967).
(10) F. P. Cavasino, *J. Phys. Chem.*, *72*, 1378 (1968).
(11) A. Ågren, *Acta Chem. Scand.*, *8*, 266 (1954).
(12) L. Vareille, *Bull. Soc. Chim. Franc.*, 872 (1955).
(13) G. F. Condike and A. E. Martell, *J. Inorg. Nucl. Chem.*, *31*, 2455 (1969).
(14) R. Foley and R. J. Anderson, *J. Am. Chem. Soc.*, *70*, 1195 (1948).

cuvette, and the variation of transmittance during the reaction, was detected on a storage Tektronix Mod. 564 oscillograph.

Results and Discussion

Equilibrium constants. The present method required the knowledge of the constants of the following equilibria:

$H_2SS^- \rightleftharpoons H^+ + HSS^{2-}$ $\quad K_{2A}$

$Fe^{3+} + HSS^{2-} \rightleftharpoons FeSS + H^+$ $\quad K_C$

$Fe^{3+} + H_2O \rightleftharpoons FeOH^{2+} + H^+$ $\quad K_{OH}$

The value of 1.65×10^{-3} *M* was assumed for K_{OH} from literature data at 1.0 *M* ionic strength,[15] even if obtained in a different ionic medium ($NaClO_4$, $HClO_4$ instead of KNO_3, HNO_3 of the present paper).

The constant K_{2A} was determined by pH metric titration of NaH_2SS with KOH. Its value, at ionic strength 1.0 *M* (KNO_3), was found to be $5.00 \pm 0.03 \times 10^{-3}$ *M*. Some experimental data, concerning the evaluation of K_{2A}, are reported in Table I.

Table I. Dissociation constant of H_2SS^-
$\mu = 1.0$ *M* (KNO_3) $\quad t = 25.0°C$

C_A m*M*	C_{KOH} m*M*	pH measd	K_{2A} $M \times 10^3$
9.96	0.5	2.332	5.00
9.96	1.5	2.396	4.99
9.96	2.5	2.467	4.98
9.96	3.5	2.545	5.02
9.96	7.0	2.947	5.02
7.97	2.0	2.524	5.02
7.97	3.0	2.621	5.01
7.97	4.0	2.736	5.03
7.97	5.0	2.883	4.97
7.97	5.9	3.057	4.98
14.9	2.0	2.278	5.03
14.9	4.0	2.383	4.99
14.9	6.0	2.502	5.01
14.9	8.1	2.655	4.98

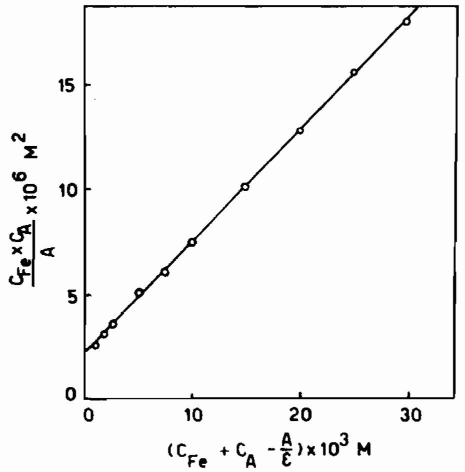


Figure 1. Plot of rearranged equation (1) for the determination of ε and K_C.

K_C was determined spectrophotometrically by using the expression:

$$K_C = \frac{(A/\varepsilon)[H^+]}{(C_{Fe} - A/\varepsilon)(C_A - A/\varepsilon)\alpha_A} \qquad (1)$$

where A = absorbance of the complex, ε = molar absorptivity, C_{Fe}, C_A = stoichiometric concentration of Fe^{III} and ligand respectively, $\alpha_A = K_{2A}/(K_{2A} + [H^+])$.

The absorbance of a series of solutions containing different ratios of Fe^{III} and ligand, was measured at $[H^+] = 0.100$ *M*, $\mu = 1.0$ *M* and $\lambda = 500$ nm. The evaluation of K_C was made by means of the method of Frank and Oswalt.[16] By neglecting $(A/\varepsilon)^2$ by respect to the other terms in the denominator of (1) and plotting $C_{Fe} \times C_A/A$ as a function of $(C_{Fe} + C_A)$, a straight line is obtained having slope $1/\varepsilon$ and intercept $[H^+]/\alpha_A K_C \varepsilon$.

By successive approximations (in order to account for the term $(A/\varepsilon)^2$), the following values of ε and K_C were obtained:

$$\varepsilon = 1.96 \pm 0.05 \times 10^3\ cm^{-1}\ M^{-1}$$

and

$$K_C = 4.87 \pm 0.10 \times 10^2$$

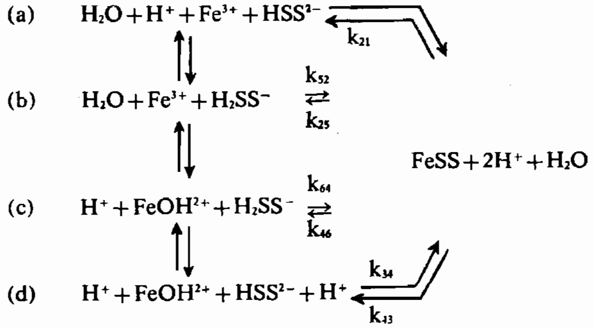
respectively, (Table II and Figure 1).

Both values do not differ appreciably from the values given by Ågren ($\mu = 3.0$ *M*, $NaClO_4$).[11]

Table II. Formation constant of Iron(III)monosulfosalicylate.
$\mu = 1.0$ *M* (KNO_3) $\quad t = 25.0°C$

C_{Fe} m*M*	C_A m*M*	A	$\frac{C_{Fe} \times C_A}{A}$ $\times 10^6\ M^2$	$C_{Fe} + C_A - \frac{A}{\varepsilon}$ $\times 10^3\ M$
5.00	0.05	0.050	5.00	5.08
10.0	0.10	0.134	7.46	10.2
20.0	0.20	0.313	12.8	20.3
30.0	0.30	0.500	18.0	30.6
0.075	7.5	0.093	6.05	7.62
0.150	15.0	0.224	10.0	15.3
0.250	25.0	0.402	15.5	25.5
0.50	0.50	0.094	2.66	1.05
1.00	1.00	0.324	3.09	2.07
1.50	1.50	0.638	3.53	3.33

Kinetics. The kinetic results are consistent with the following reaction scheme:



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(15) R. M. Milburn, *J. Am. Chem. Soc.*, 79, 537 (1957).

(16) H. S. Frank and R. L. Oswalt, *J. Am. Chem. Soc.*, 69, 1321 (1947).

This scheme is in the form given by Accascina, Cavasino and d'Alessandro for the reaction between Fe^{III} and N_3^-,[9] assuming that the intermediate species $FeOH–H_2SS^+$ and FeOH–HSS of the reactions (c) and (d) are in a steady state (this hypothesis is justified if protonation and deprotonation reactions are considered faster than complex formation reactions).

The reaction rate is given by:

$$\frac{d[FeSS]}{dt} = k_{12}[Fe^{3+}][HSS^{2-}]-k_{21}[FeSS][H^+]+ k_{52}[Fe^{3+}][H_2SS^-]-k_{25}[FeSS][H^+]^2+k_{64}[FeOH^{2+}][H_2SS^-]- k_{46}[FeSS][H^+]+k_{34}[FeOH^{2+}][HSS^{2-}]-k_{43}[FeSS] \quad (2)$$

If the above assumption about protonation and deprotonation reactions (vertical arrows in the above scheme) is made, it follows:

$$\frac{d[FeSS]}{dt} = \left(k_{12}+k_{52}\frac{[H^+]}{K_{2A}} + k_{64}\frac{K_{OH}}{K_{2A}} + k_{34}\frac{K_{OH}}{[H^+]}\right)\times [Fe^{3+}][HSS^{2-}]-(k_{21}[H^+]+k_{25}[H^+]^2+k_{46}[H^+]+k_{43})[FeSS]\cdot \quad (3)$$

At equilibrium $d[FeSS]/dt = 0$; therefore:

$$\frac{d[FeSS]}{dt} = \left(k_{12}+k_{52}\frac{[H^+]}{K_{2A}} + k_{64}\frac{K_{OH}}{K_{2A}} + k_{34}\frac{K_{OH}}{[H^+]}\right)\times \left([Fe^{3+}][HSS^{2-}] - \frac{[Fe^{3+}]_{eq}[HSS^{2-}]_{eq}}{[FeSS]_{eq}}[FeSS]\right) \quad (4)$$

Taking into account that:

$$C_A = \frac{[HSS^{2-}]}{\alpha_A} + [FeSS] = \frac{[HSS^{2-}]_{eq}}{\alpha_A} + [FeSS]_{eq} \quad (5)$$

and that in the presence of an excess of $[H^+]$ and Fe^{III}, ($[FeOH^{2+}]$ can be neglected) $C_{Fe} \simeq [Fe^{3+}] \simeq [Fe^{3+}]_{eq}$, we have:

$$\frac{d[FeSS]}{dt} = \left(k_{12}+k_{52}\frac{[H^+]}{K_{2A}} + k_{64}\frac{K_{OH}}{K_{2A}} + k_{34}\frac{K_{OH}}{[H^+]}\right)\times \left(C_{Fe}\alpha_A + \frac{[H^+]}{K_C}\right)\left([FeSS]_{eq}-[FeSS]\right) \quad (6)$$

In the case of an excess of ligand, equation (6) contains $\left(\frac{C_A \, . \, \alpha_A}{1+K_{OH}/[H^+]} + \frac{[H^+]}{K_C}\right)$ instead of $\left(C_{Fe}\alpha_A + \frac{[H^+]}{K_C}\right)$. These factors will be later indicated with B.

So, the reaction rate, in the presence of an excess of one reagent, can be given by the pseudo first order expression:

$$d[FeSS]/dt = k_{obs}([FeSS]_{eq}-[FeSS]) \quad (7)$$

Some experimental values of k_{obs}, as determined by the slope of the plot of $\ln \frac{[FeSS]_{eq}}{[FeSS]_{eq}-[FeSS]}$ as a function of time, are collected in Table III.

Figure 2 gives a typical plot of experimental data.

From (6) and (7):

$$k_{obs}/B = k_{12}+k_{52}[H^+]/K_{2A}+k_{64}K_{OH}/K_{2A}+k_{34}K_{OH}/[H^+] \quad (8)$$

By plotting the average values of k_{obs}/B (for measurements in the presence of an excess of Fe^{III} or of the ligand) as a function of $1/[H^+]$, the diagram given in Figure 3 was obtained. Average values of k_{obs}/B are listed in Table IV.

Table III. Kinetic data for FeSS formation.
$\mu = 1.0\,M$ (KNO_3) t = 25.0°C

C_{Fe} m*M*	C_A m*M*	$[H^+]$ *M*	k_{obs} sec^{-1}	k_{obs}/B $\times 10^{-3}$ M^{-1} sec^{-1}
30.0	0.20	0.500	2.7	2.0
20.0	0.20	0.500	2.5	2.0
10.0	0.20	0.500	2.3	2.0
5.0	0.20	0.500	2.2	2.0
30.0	0.20	0.200	2.3	2.0
25.0	0.20	0.200	2.1	2.1
20.0	0.20	0.200	1.8	2.0
15.0	0.20	0.200	1.6	2.1
10.0	0.20	0.200	1.3	2.0
7.5	0.20	0.200	1.2	2.0
5.0	0.20	0.200	1.1	2.1
0.20	20.0	0.200	1.8	2.0
0.20	25.0	0.025	9.9	2.5
0.20	15.0	0.025	6.4	2.7
0.20	10.0	0.025	4.2	2.7
0.20	7.5	0.025	3.0	2.6
0.20	12.5	0.010	14	3.9
0.20	10.0	0.010	11	3.8
0.20	8.0	0.010	8.6	3.8
0.20	4.0	0.010	4.4	3.8

Table IV. Average values of k_{obs}/B

$[H^+]$ *M*	$k_{obs}/B \times 10^{-3}$ M^{-1} sec^{-1}
0.500	2.0
0.300	2.0
0.200	2.0
0.100	2.0
0.025	2.6
0.020	2.8
0.015	3.2
0.010	3.8

Accascina and coworkers,[9,10] remarked that equation (8) should hold for the kinetics of complexation of Fe^{III} with various ligands and that k_{obs}/B should be minimum for a value of $[H^+]$ given by $(k_{34}K_{OH}K_{2A}/k_{52})^{1/2}$.

They also tabulated the values found by different authors for the kinetic constants k_{34} and k_{52}. This latter ranges from 4 to 51 M^{-1} sec^{-1}, whereas the former ranges from 1 to 24×10^4 M^{-1} sec^{-1}.

By attributing to the above constants, in the present reaction, values of the order of 10^1 and 10^5 M^{-1} sec^{-1} respectively, the minimum should lie in the range of $[H^+] = 0.2 \div 0.4\,M$.

The curve obtained from experimental data, shows a clear flatness in this region.

Since the plot of k_{obs}/B versus $1/[H^+]$ (Figure 3), is not linear over the whole hydrogen ion concentration range covered, it is possible to deduce that the term $k_{52}[H^+]/K_{2A}$ is not negligible with respect to the other terms (see eq. 8), in the region of higher acidities, as expected from the reaction mechanism proposed.

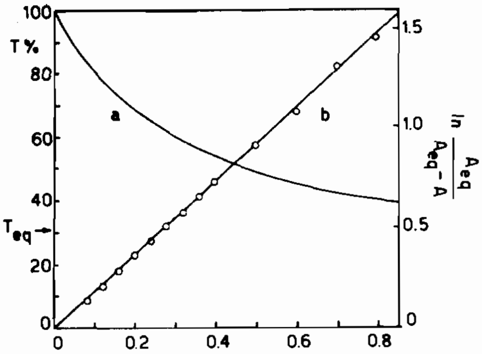

Figure 2. (a) Experimental variation of transmittance T (ordinates at left) as a function of time. (C_{Fe} = 15.0 m*M*, C_A = 0.20 m*M*, $[H^+]$ = 0.100 *M*). (b) Plot of data of curve a) according to first order kinetics (ordinates at right) as a function of time.

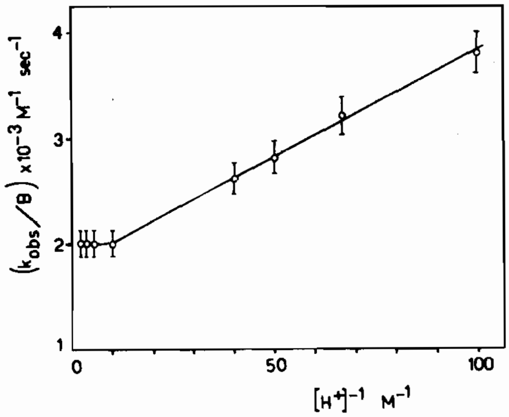

Figure 3. Dependence of k_{obs}/B as a function of $[H^+]^{-1}$

Additional measurements have not been performed at $[H^+]$ higher than 0.5 *M*, because so high hydrogen ion concentrations strongly decrease the conditional stability constant of the complex, and make possible the formation of undissociated sulphonic groups.

Under these hypotheses, the curve which gives the best approximation with the experimental values should be the following:

$$k_{obs}/B = 3.0\times 10^2[H^+]+1.8\times 10^3 + \frac{2.0\times 10^1}{[H^+]} \qquad (9)$$

Using the data of equation (9) and referring to equation (8), the following kinetic constants were found:

$$k_{52} = 1.5\pm 1\ M^{-1}\ sec^{-1} \qquad k_{34} = 1.2\pm 0.1\times 10^4\ M^{-1}\ sec^{-1}$$

$$\left(k_{12}+k_{64}\frac{K_{OH}}{K_{2A}}\right) = 1.8\pm 0.2\times 10^3\ M^{-1}\ sec^{-1}$$

The values of k_{52} and k_{34} are of the order of the constants listed in the table given by Accascina and coworkers[9] for the kinetics of reaction of Fe^{III} with various ligands, and show that reaction (b) contributes appreciably to the formation of FeSS only in strongly acidic mediums.

Turning now to the reactions (a) and (c), it is not possible from experimental data an evaluation of the constants k_{12} and k_{64}, owing to the independence of pH of both reactions.

This point was already discussed by Accascina and coworkers, who came to the conclusion that reaction (a) is rate determining only for ligands which exibit very weakly basic properties, because in this case the term $k_{64}K_{OH}/K_{2A}$ becomes small compared to k_{12}, owing to the fact that k_{64} and k_{12} seem to be largely independent of the properties of ligand, and the kinetic constants of $FeOH^{2+}$ are of about three orders higher than those of Fe^{III}.[1,2,3,4,7]

In the present case, the coefficient K_{OH}/K_{2A} is 0.33 and therefore it could be expected that reaction (c) should give a large contribution to the formation of FeSS.

In this hypothesis, k_{64} should be of the order of $10^3\,M^{-1}$ sec^{-1} in agreement with the literature data for other ligands such as F^-, and N_3^-,[4,7] which have about the same basicity of our ligand.

Another criterion for the evaluation of the contribution of the single terms independent of $[H^+]$, was recently suggested by Cavasino.[10] Taking into account that k_{34} must be higher than k_{64}, owing to the fact that the reaction takes place between the ion $FeOH^{2+}$ and a species with charge −2 in respect of a species with charge −1, it is possible to exclude a significant contribution to the term $k_{64}K_{OH}/K_{2A}$ if the value of k_{64} calculated from experimental data is higher than k_{34}.

Our data show that $k_{34}/k_{64} \simeq 2$; therefore the experimental data are in agreement with the hypothesis that the complex formation proceeds essentially in accordance with reactions (c) and (d) of the above scheme.

The possible contribution of the reaction (a) to the complex formation could be considered as a sequence of elementary steps as suggested by Eigen,[17] who assumed that the ion pair formed in the first kinetic stage of complexation, could undergo an « inner hydrolysis » which increases with the basicity of the reacting ligand.

This means in our case, that $Fe(H_2O)_6^{3+}$ associated as ion pair with HSS^{2-}, could rapidly loose H^+, accepted by the ligand, giving $Fe(H_2O)_5OH^{2+}-H_2SS^-$, which then reacts with formation of the inner complex and elimination of a water molecule.

Some authors, by making approximate assumptions, have evaluated the constants of the various elementary steps of the complexation of Fe^{III} with mono and bidentate ligands.

In order to calculate the ion pair formation constant, the Fuoss relation has been often used.[18] Since such relation approximates the reacting species to charged spherical entities, its application to the pre-

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[17] M. Eigen in « Advances in the Chemistry of the Co-ordination Compounds » Ed. S. Kirschner, The Macmillan Co., New York, N. Y., 1961, p. 371.

[18] R. M. Fuoss, *J. Am. Chem. Soc.*, *80*, 5059 (1958).

sent ligand should presumably bring to unreliable values, as found by Geier in an investigation of the kinetics of reaction of metal ions with purpuric acid.[19]

Therefore we will confine ourselves to point out that the constants k_{64} and k_{34}, are of the same order of magnitude of the rate constant of exchange of a water molecule between water in bulk and the $Fe(H_2O)_5OH^{2+}$ ion.[20]

This supports the results found by several authors for the kinetics of reaction of aquated iron(III) with basic ligands.

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(19) G. Geier, *Helv. Chim. Acta, 51,* 94 (1968).

(20) R. E. Connick and E. E. Genser, quoted in Ref. (7).