Reactions between Iron(III) and Catechol (*o*-Dihydroxybenzene). Part I. Equilibria and Kinetics of Complex Formation in Aqueous Acid Solution

By **Edoardo Mentasti** * and **Ezio Pelizzetti**, Istituto di Chimica Analitica, Università di Torino, Italy

The equilibria and kinetics of formation of catecholato(2−)iron(III) have been studied over the pH range 1·00—2·00 in aqueous media with the stopped-flow technique. At 25·0 °C and ionic strength 1·0M ($NaClO_4$), the equilibrium constant K_c for chelate-complex formation (i) is (4·35 ± 0·10) × 10^{-2} mol l^{-1} and $\varepsilon[Fe(cat)^+] = (1{\cdot}25 \pm 0{\cdot}05) \times 10^3$ l mol^{-1} cm^{-1} at 700 nm. From the hydrogen-ion dependence of the reaction rate it can be shown that complex

$$Fe^{3+} + H_2cat \rightleftharpoons [Fe(cat)]^+ + 2H^+ \qquad (i)$$

formation occurs between $[FeOH]^{2+}$ ion and catechol with a rate constant $k = (3{\cdot}1 \pm 0{\cdot}2) \times 10^3$ l mol^{-1} s^{-1}; estimated activation data are $\Delta H^\ddagger = 9{\cdot}6 \pm 1{\cdot}0$ kcal mol^{-1} and $\Delta S^\ddagger = -11{\cdot}1 \pm 3{\cdot}0$ cal K^{-1} mol^{-1}. The experimental data are consistent with the accepted I_d mechanism for ligand substitution.

IN a previous paper the kinetics of iron(III) complex formation with salicylic acid[1] was investigated in an acidic aqueous medium. In order to investigate the effect of a positive or negative charge on the ligand in such reactions, further work concerned the kinetics of reaction of iron(III) with *p*-aminosalicylic[2] and 5-sulphosalicylic acid[3] under the same experimental conditions. It then seemed of some interest to study the complex-formation equilibria and kinetics of reaction between iron(III) and catechol (*o*-dihydroxybenzene), a ligand able to form a chelate ring through attachment of two identical groups (*i.e.* $-O^-$ groups). Moreover, kinetic data for this reaction could be compared with data obtained for the corresponding reaction with phenol,[4] so as to determine whether the chelate ring-closure step makes an appreciable contribution to the overall complex-formation rate.[5] The complex-formation reaction between iron(III) and catechol is followed by a redox reaction giving iron(III) and an oxidation product of catechol. The equilibria and kinetics of the redox reaction are discussed in the following paper.

EXPERIMENTAL

Stock solutions of perchloric acid and sodium perchlorate, used for adjusting the hydrogen-ion concentration and ionic strength (all experiments were performed at ionic strength $I = 1{\cdot}0$M), were prepared by dissolving in doubly distilled water the corresponding analytical grade chemicals (C. Erba RP). Fresh catechol solutions were prepared daily by dissolving weighed amounts of the solid (C. Erba RP) in doubly distilled and freshly boiled water. The solutions were protected from direct light in order to avoid decomposition reactions. An acidic stock solution of iron(III) perchlorate was prepared from perchloric acid and iron(III) perchlorate (C. Erba R). The latter reagent was previously recrystallized from aqueous perchloric acid. Iron(III) concentrations were determined by complexometric titration; hydrogen-ion concentrations were evaluated from iron(III) concentrations and total $[H^+]$ after exchange on a Dowex 50 W (H^+ form) resin.

The instruments used were as described previously.[3] All measurements were made at 20·0, 25·0, and 30·0 °C.

RESULTS AND DISCUSSION

Evaluation of the equilibrium data for complex formation between iron(III) and catechol was made using a

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[1] G. Saini and E. Mentasti, *Inorg. Chim. Acta*, 1970, **4**, 585.

[2] E. Mentasti and G. Saini, *Atti Accad. Sci. Torino*, 1971—1972, **106**, 501.

[3] G. Saini and E. Mentasti, *Inorg. Chim. Acta*, 1970, **4**, 210.

[4] F. P. Cavasino and E. Di Dio, *J. Chem. Soc.* (*A*), 1970, 1151.

[5] H. Hoffmann, *Ber. Bunsengesellschaft Phys. Chem.*, 1969, **73**, 432.

stopped-flow spectrophotometer; with this technique it was possible to perform equilibrium spectrophotometric measurements before the subsequent redox reaction could take place, and to obtain the absorption spectrum of the complex from 350 to 750 nm. The spectra at pH 1·00 and 2·00 (Figure 1) showed a similar trend with a flat maximum at 700 nm, suggesting that, in this pH range, the absorption is due to the same absorbing species. Figure 1 also shows the spectrum of the product after completion of the redox reaction; it consists of an absorption maximum at 390 nm, in the expected position for *o*-quinone.[6,7] Moreover preliminary experiments, where 1,10-phenanthroline was added as indicator to the above reaction mixture, showed the occurrence of iron(II) ions as a product of the redox reaction. Figure 2 shows the variation of transmittance, at 700 nm, as a function of time for a typical run; the different time scales show the fast complex formation and slower complex disappearance, due to the redox reaction. A kinetic run performed at 508 nm showed that iron(II) formation proceeds at the same rate as that of *o*-quinone formation.

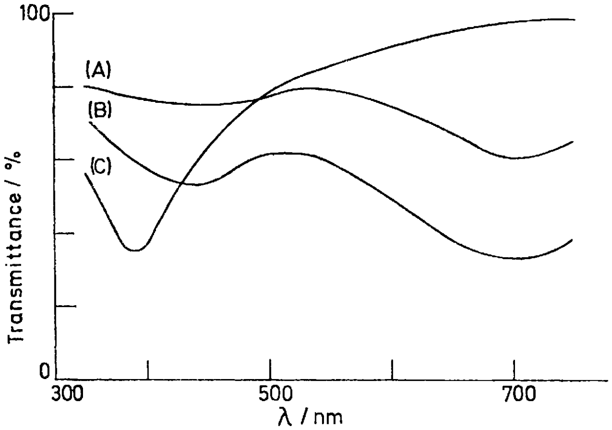

FIGURE 1 Spectra of the complex $[Fe(cat)]^+$ (A, B) and the oxidation product of catechol (C): (A) $c_A = 2{\cdot}00 \times 10^{-2}$, $c_{Fe} = 1{\cdot}00 \times 10^{-3}$M, pH = 1·00; (B) $c_A = 1{\cdot}25 \times 10^{-2}$, $c_{Fe} = 2{\cdot}0 \times 10^{-4}$M, pH 2·00; and (C) $c_A = 2{\cdot}00 \times 10^{-2}$, $c_{Fe} = 4{\cdot}0 \times 10^{-4}$M, pH 1·00

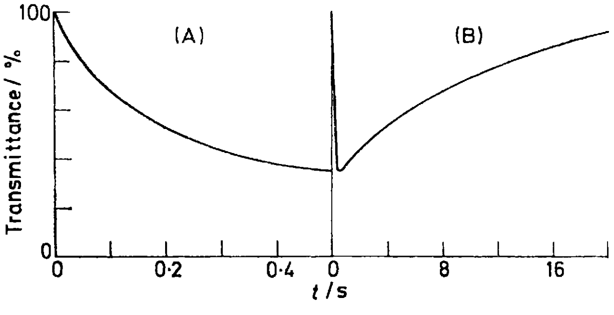

FIGURE 2 Oscilloscope traces for $[Fe(cat)]^+$ formation (A) and disappearance (B) at 700 nm: $c_A = 8{\cdot}00 \times 10^{-3}$, $c_{Fe} = 4{\cdot}0 \times 10^{-4}$, $[H^+] = 0{\cdot}020$M

Complex-formation Equilibrium.—The catechol (H_2cat) and iron(III) concentrations used and the hydrogen-ion range investigated (from pH 1·00 to 2·00) were so chosen that the extent of complex formation was such as to allow good accuracy in spectrophotometric data evaluation and so that the only product of hydrolysis of Fe^{3+}, present in appreciable concentration, was $[FeOH]^{2+}$. Under these experimental conditions, equilibria (1) and (2) are relevant. Values of K_{OH} were estimated to be $1{\cdot}23 \times 10^{-3}$, $1{\cdot}65 \times 10^{-3}$, and $2{\cdot}19 \times 10^{-3}$ mol l^{-1} respectively at 20·0, 25·0, and 30·0 °C from ref. 8. Catechol was assumed to be completely undissociated at the pH investigated, according to its dissociation constants.[9] The equilibrium constant K_c was evaluated spectrophotometrically.

$$Fe^{3+}(aq) \underset{}{\overset{K_{OH}}{\rightleftharpoons}} [FeOH]^{2+}(aq) + H^+(aq) \qquad (1)$$

$$Fe^{3+}(aq) + H_2cat(aq) \overset{K_c}{\rightleftharpoons} [Fe(cat)]^+(aq) + 2H^+(aq) \qquad (2)$$

Two solutions, containing respectively iron(III) and catechol (in excess) brought to the same ionic strength and pH, were mixed in a stopped-flow spectrophotometer and the transmittance of the mixture was recorded at 700 nm as a function of time. With this procedure data concerning the transient equilibrium [which takes place after completion of complex formation and before commencement of the redox reaction (see Figure 2), could be evaluated. For these equilibrium measurements, carried out at $0{\cdot}100 \geqslant [H^+] \geqslant 0{\cdot}010$M, the concentration of catechol (c_A) ranged from $6{\cdot}0 \times 10^{-3}$ to $4{\cdot}0 \times 10^{-2}$M, whereas the concentration of iron(III) (c_{Fe}) ranged from $3{\cdot}0 \times 10^{-4}$ to $1{\cdot}0 \times 10^{-3}$M.

Assuming that the only complex species present in solution is $[Fe(cat)]^+$, and that it is the only absorbing species at 700 nm, equations (3) and (4) follow, where A

$$c_{Fe} = [Fe^{3+}] + [FeOH^{2+}] + [Fe(cat)^+] \qquad (3)$$

$$A(700\ \text{nm}) = \varepsilon l[Fe(cat)^+] \qquad (4)$$

is the absorbance, ε the absorption coefficient of the complex at 700 nm, and l the path length (2·00 cm). By taking into account the expressions for K_c and K_{OH} defined by equations (1) and (2) and using (3) and (4), equation (5) can be obtained. By plotting c_{Fe}/A as a

$$c_{Fe}/A = 1/\varepsilon l + (1/\varepsilon l K_c)\frac{([H^+]+K_{OH})[H^+]}{[c_A - (A/\varepsilon l)]} \qquad (5)$$

function of $([H^+] + K_{OH})[H^+]/c_A$, with successive approximations in order to take into account the term $A/\varepsilon l$, linear behaviour was obtained. In Figure 3 a plot obtained according to equation (5) is shown for measurements at 25·0 °C. The same trend was found at 20·0 and 30·0 °C. The linearity of the plots supports

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[6] S. W. Weidman and E. T. Kaiser, *J. Amer. Chem. Soc.*, 1966, **88**, 5820.

[7] H. S. Mason, *J. Biol. Chem.*, 1949, **181**, 803.

[8] R. M. Milburn, *J. Amer. Chem. Soc.*, 1957, **79**, 537.

[9] 'Stability Constants of Metal-ion Complexes,' eds. L. G. Sillén and A. E. Martell, Chem. Soc. Special Publ. no. 17, 1964.

the assumption of the presence, under these experimental conditions, of only the complex [Fe(cat)]$^+$. Table 1 lists values of the equilibrium constant K_c and the absorption coefficient for [Fe(cat)]$^+$ formation.

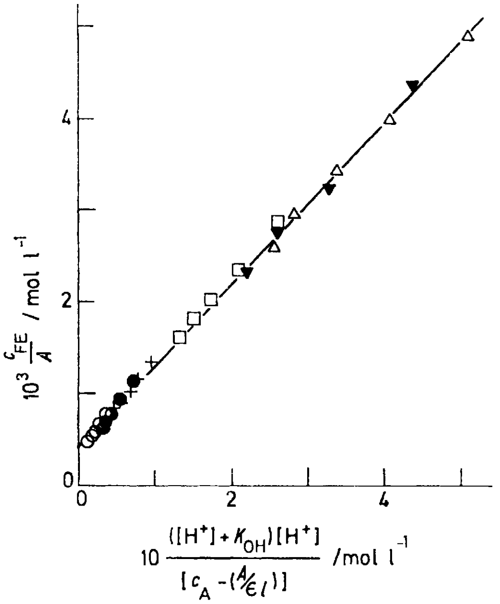


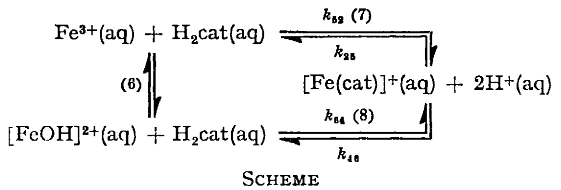
FIGURE 3 Plot of experimental data, according to equation (5), for the evaluation of ε and K_C: $[H^+] = 0{\cdot}014$ (○); 0·020 (●); 0·030 (+); 0·050 (□); 0·080 (▼); and 0·100M (△)

TABLE 1

Equilibrium constants and absorption coefficients for [Fe(cat)]$^+$ formation: I = 1·0M (NaClO$_4$)

t/°C	20·0	25·0	30·0
K_c/mol l^{-1}	(4·26 ± 0·10) × 10^{-2}	(4·35 ± 0·10) × 10^{-2}	(4·46 ± 0·10) × 10^{-2}
ε/l mol^{-1} cm^{-1}	(1·20 ± 0·05) × 10^3	(1·25 ± 0·05) × 10^3	(1·30 ± 0·05) × 10^3

Complex-formation Kinetics.—Under the experimental conditions investigated, the following scheme can be assumed.



SCHEME

Reaction (6) concerns a protolytic process which can be assumed to be very fast compared to the complex-formation reactions,[10] and pseudo-first-order kinetics can be shown to hold if the catechol concentration is in an excess over that of iron(III). From the Scheme the rate complex formation can be expressed by equation (9). By taking into account the equilibrium conditions equation (10) is obtained. Now, taking into

$$d[Fe(cat)^+]/dt = k_{52}[Fe^{3+}][H_2cat] + k_{64}[FeOH^{2+}][H_2(cat)] - k_{25}[Fe(cat)^+][H^+]^2 - k_{46}[Fe(cat)^+][H^+] \quad (9)$$

$$\frac{d[Fe(cat)^+]}{dt} = \left(k_{52} + k_{64}\frac{K_{OH}}{[H^+]}\right)[Fe^{3+}][H_2cat] - \left(k_{52} + k_{64}\frac{K_{OH}}{[H^+]}\right)[Fe(cat)^+]\frac{[Fe^{3+}]_{eq}[H_2cat]_{eq}}{[Fe(cat)^+]_{eq}} \quad (10)$$

account equation (11), and that $[H_2cat] \simeq [H_2cat]_{eq}$

$$c_{Fe} = [Fe^{3+}] + [FeOH^{2+}] + [Fe(cat)^+] = [Fe^{3+}]_{eq} + [FeOH^{2+}]_{eq} + [Fe(cat)^+]_{eq} \quad (11)$$

(reactant present in excess) and $[H^+] \simeq [H^+]_{eq}$ (because, under the experimental conditions, the hydrogen-ion concentration does not appreciably change during complex formation), integrated equation (12) can be obtained, which corresponds to the rate of a

$$\ln \frac{[Fe(cat)^+]_{eq}}{([Fe(cat)^+]_{eq} - [Fe(cat)^+])} = \left(k_{52} + k_{64}\frac{K_{OH}}{[H^+]}\right)\left(c_A\frac{[H^+]}{[H^+] + K_{OH}} + \frac{[H^+]^2}{K_c}\right)t \quad (12)$$

pseudo-first-order reaction. The experimental pseudo-first-order rate constant, is given by equation (13).

$$k_{obs} = \left(k_{52} + k_{64}\frac{K_{OH}}{[H^+]}\right)B \quad (13)$$

where $B = \left(c_A\frac{[H^+]}{[H^+] + K_{OH}} + \frac{[H^+]^2}{K_c}\right)$

Figure 4 shows plots of k_{obs}/B as a function of $[H^+]^{-1}$ at 20·0, 25·0, and 30·0 °C, each point representing the average value from about five runs at different c_A values (*i.e.* different B values). The plots are linear and their intercept does not differ significantly from zero. Experimental data concerning the kinetic runs are collected in Table 2. The absence of an intercept in Figure 4 indicates that the term k_{52} in equation (13) can be neglected;

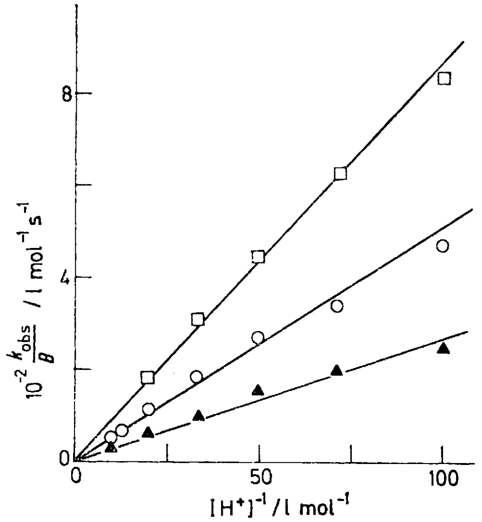


FIGURE 4 Inverse hydrogen-ion dependence of k_{obs}/B for [Fe(cat)]$^+$ complex formation at 20·0 (▲), 25·0 (○), and 30·0 °C (□)

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[10] M. Eigen and L. de Maeyer, ' Technique of Organic Chemistry,' eds. S. L. Friess, E. S. Lewis, and A. Weissberger, Interscience, New York, 1963, p. 895.

that is complex formation takes place essentially through reaction (8), whereas reaction (7) does not contribute appreciably. k_{64} Values are reported in Table 3 together with estimates of $\Delta H^‡$ and $\Delta S^‡$. The results are in agreement with previous experimental evidence that the ion $[Fe(H_2O)_5OH]^{2+}$ reacts with rates 10^3 times higher than $[Fe(H_2O)_6]^{3+}$;[11] moreover, in the present case, a reaction mechanism involving 'inner hydrolysis'[12] seems improbable because of the small basicity of the reacting ligand. The experimental dependence of reaction rate on hydrogen-ion concentration seems to suggest that $[Fe(H_2O)_5OH]^{2+}$ ion is the true reacting species. Therefore the reaction mechanism appears to be a sequence of paths (6) (fast protolytic reaction) and (8).

TABLE 2

Kinetic data for $[Fe(cat)]^+$ formation: $I = 1{\cdot}0$M ($NaClO_4$)

$[H^+]$/M	10^3c_A/M	10^3c_{Fe}/M		k_{obs}/s^{-1}	
			(20·0 °C)	(25·0 °C)	(30·0 °C)
0·010	6·0	0·20	2·26	3·80	6·33
0·010	8·0	0·20	2·61	4·36	7·43
0·010	10·0	0·20	2·84	5·24	8·37
0·010	12·5	0·20	3·09	5·71	10·4
0·010	15·0	0·20	3·57	6·68	11·6
0·014	6·0	0·30	2·26	3·65	6·2
0·014	8·0	0·30	2·42	4·07	7·34
0·014	10·0	0·30	2·59	4·50	8·14
0·014	12·5	0·30	2·97	4·97	9·7
0·014	15·0	0·30	3·24	5·60	10·2
0·020	6·0	0·40	2·41	4·20	6·88
0·020	8·0	0·40	2·74	4·78	7·48
0·020	10·0	0·40	2·96	4·96	8·35
0·020	12·5	0·40	2·99	4·16	8·65
0·020	15·0	0·40	3·28	5·84	9·98
0·030	10·0	0·50	3·46	5·87	9·80
0·030	12·5	0·50	3·50	6·09	9·96
0·030	15·0	0·50	3·58	6·06	10·4
0·030	17·5	0·50	3·80	6·77	10·9
0·030	20·0	0·50	3·92	7·09	11·1
0·050	10·0	0·60	4·26	7·30	12·7
0·050	12·5	0·60	4·35	7·60	11·9
0·050	15·0	0·60	4·58	7·55	13·2
0·050	17·5	0·60	4·58	8·11	13·1
0·050	20·0	0·60	4·93	8·84	12·8
0·080	10·0	0·80		9·81	
0·080	15·0	0·80		9·95	
0·080	20·0	0·80		9·93	
0·080	25·0	0·80		10·9	
0·080	30·0	0·80		11·4	
0·100	20·0	1·00	7·75	12·7	
0·100	25·0	1·00		13·1	
0·100	30·0	1·00		13·3	
0·100	35·0	1·00		13·8	
0·100	40·0	1·00		13·8	

TABLE 3

Rate constant and activation parameters for $[Fe(cat)]^+$ formation: $I = 1{\cdot}0$M ($NaClO_4$)

t/°C	20·0	25·0	30·0
k_{64}/l mol^{-1} s^{-1}	$(2{\cdot}3 \pm 0{\cdot}1) \times 10^3$	$(3{\cdot}1 \pm 0{\cdot}2) \times 10^3$	$(4{\cdot}0 \pm 0{\cdot}2) \times 10^3$
$\Delta H^‡$/kcal mol^{-1}		$9{\cdot}6 \pm 1{\cdot}0$	
$\Delta S^‡$/cal K^{-1} mol^{-1}		$-11{\cdot}1 \pm 3{\cdot}0$	

By comparing rates found for the present reaction with those found for previously examined ligands at the same temperature and ionic strength, it follows that the present reaction has a smaller specific rate constant but one of the same order of magnitude; this is in agreement with the fact that complex-formation reactions of iron(III) have been generally found to follow an S_N1 mechanism involving loss of water molecules from the co-ordination sphere of the metal ion in the rate-determining step. Thus k_{64} can be compared with the corresponding rate of reaction of iron(III) with phenol ($1{\cdot}5 \times 10^3$ l mol^{-1} s^{-1}). The latter value is about half the former; in order to explain the factor of 2 one could take into account that the catechol hydroxy groups have twice the chance of that of phenol in displacing the first water molecule in the co-ordination sphere of the ion $[Fe(H_2O)_5OH]^{2+}$ for inner-sphere complex formation. However the different ion–dipole interactions of the two ligands with $[Fe(H_2O)_5OH]^{2+}$ in the outer-sphere complex-formation equilibrium could make a significant contribution to the rate of reaction (8). If this difference in rate can be interpreted as a statistical factor, it follows that the step of chelate closure in the case of catechol cannot be rate determining.

Rate constants found for iron(III) complex formation with various ligands such as Cl^-,[13] Br^-,[13] SO_4^{2-},[14,15] HN_3,[16] salicylic acid,[1] 5-sulphosalicylic acid,[3] *p*-aminosalicylic acid,[2] phenols,[4] oxalic acid,[17] mandelic acid,[18] *etc.* are of the same order of magnitude in spite of the different structure, basicity, and chelation capability; small differences can be explained in terms of different charges and sizes of the reacting species, that is taking into account the outer-sphere complex-formation constant which contributes to the overall specific rate constants.[19] Also a comparison of estimated $\Delta H^‡$ and $\Delta S^‡$ values shows that the mechanism of complex formation for iron(III) is independent of the entering ligand. This suggests that reaction occurs through a dissociative I_d mode,[20] that is the entering ligand has no appreciable influence on the preceding loss of water molecules from the co-ordination sphere of the metal ion.

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[3/550 *Received*, 15*th March*, 1973]

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