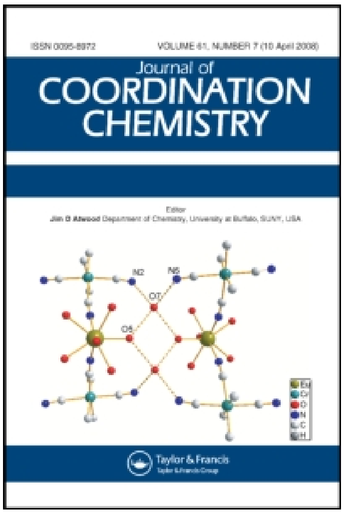

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THE EQUILIBRIA AND KINETICS OF THE COMPLEX FORMATION BETWEEN Fe(III) AND TARTARIC AND CITRIC ACIDS

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THE EQUILIBRIA AND KINETICS OF THE COMPLEX FORMATION BETWEEN Fe(III) AND TARTARIC AND CITRIC ACIDS

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The equilibria and kinetics of formation of 1 : 1 iron(III) complexes with tartaric and citric acids have been studied in the pH range 1.0–2.0 in aqueous alcoholic perchlorate media. The equilibrium constants for the reactions $Fe^{3+} + H_4L \overset{k_{eq}}{\rightleftharpoons}$ Complex $+ nH^+$ were obtained from spectrophotometric measurements in the wavelength range 360–420 nm. The values of K_{eq} determined at 20°, $\mu = 1.0$ M (water 100%), were 0.21 M with $n = 2$ for tartaric and 0.0186 M^2 with $n = 3$ for citric acid. The stoichiometry of the complex formation and the reaction sites of the ligands were discussed with reference to previous findings on ligands of related structures. The kinetics of the reactions were carried out by the stopped-flow technique. From the hydrogen ion dependence of the reaction rates it can be shown that complex formation occurs between $FeOH^{2+}$ and differently protonated forms of the ligands. Forward rates for the different paths are consistent with an SN1 IP interaction in agreement with the Eigen mechanism; forward and reverse rate quotients enabled the evaluation of the equilibrium constants which agreed satisfactorily with the spectrophotometric ones. The effect of varying the solvent composition (water–alcohol) was discussed with reference to the reaction mechanism.

INTRODUCTION

Complex formation of iron(III) with polydentate ligands[1] in aqueous solution has been generally found to occur in a multiple step mechanism:

$$Fe(H_2O)_6^{3+} + L \xrightleftharpoons{\text{fast}} Fe(H_2O)_6,L^{3+} \quad \text{(outer-sphere complex)} \qquad (1)$$

$$Fe(H_2O)_6,L^{3+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Fe(H_2O)_{6-1}L^{3+} + H_2O \quad \text{(monodentate complex)} \qquad (2)$$

$$Fe(H_2O)_{6-1}L^{3+} \xrightarrow{\text{fast}} Fe(H_2O)_{6-n}L^{3+} + (n-1)H_2O \quad (n\text{-dentate complex}) \qquad (3)$$

The above sequence, namely the Eigen mechanism,[2] involves a fast ion pair formation, with an association constant whose magnitude is related to the charges of the reacting pair and the geometry of the ion pair in the prevailing medium (*i.e.* electrostatic interactions are predominant and no chemical effect arises from the nature of the participating ligand).[3] The rate determining step in the above mechanism is the first water molecule release from the inner coordination sphere of the metal before the penetration of the ligand (step (2)).[4] Thus, also this step should not be affected by the ligand structure and its rate should be governed by the typical water exchange rate at the coordination sphere of the aquometal ion.[4]

This is a general scheme for complex formation mechanisms at labile metal ions, which however in the case of Fe(III) can be complicated by some ligand effects.[5] It is well established that substitution at the hydrolyzed metal ion is faster than at the unhydrolyzed one thus the basicity and structure of the ligand could play important effects such as in the "internal conjugate base" (ICB)[5] mechanism or to promote a sterically controlled substitution.[6]

According to the above mechanism the observed rate constant equals K_0k^* (where K_0 is the equilibrium constant for the outer-sphere complex formation and k^* is the first order water exchange rate at the metal ion). In the case of polydentate ligands ring closure steps, following the first penetration, are faster and no kinetic effect is observed unless some retardations are operated by the unavailability of the ligand groups such as in the case of internally hydrogen bonded carboxylic or hydroxy groups,[7] or by special steric or conformational requirements.[8]

Pursuing previous investigations on simple α-OH-carboxylic acids, such as glycolic, lactic, malic and benzilic acids,[1] results are now reported on the equilibria, mechanism and kinetics of Fe(III) with two hydroxycarboxylic ligands, namely tartaric and citric acids.

It has been pointed out that also at *p*H lower than 2.0 α-OH-carboxylic acids act as bidentate ligands and Fe(III) displaces both carboxylic and alcoholic protons. In the case of tartaric acid and citric acid, the α-OH-COOH moiety is still present but additional coordinating sites are present so that it seemed of interest to investigate if the alkoxide group could still play a role in the complex formation.

Both kinetic and equilibrium measurements were performed in order to clarify these points.

EXPERIMENTAL

Materials. – L(+)Tartaric and citric acids (C. Erba) were reagent grade chemicals. Stock solutions of the acids were standardized by *p*H metric titrations. Fe(III) was used in the form of $Fe(ClO_4)_3.6H_2O$ (Alfa Reagent Grade). A 10^{-2} M stock solution was prepared, containing 10^{-1} M perchloric acid and standardized by EDTA titration. Perchloric acid and sodium perchlorate (E. Merck) stock solutions were used to bring all the solutions to the desired acidity and ionic strength ($\mu = 1.0$ M). Equilibrium and kinetic measurements were performed at 8.0° and 20.0 °C and in water, methanol (MeOH) or *n*-propanol (*n*PrOH) aqueous mixtures.

Equilibrium Constants. – K_h, the hydrolysis constant for $FeOH^{2+}$ formation, has been computed from Milburn data[9] to be 6.0×10^{-4} and 1.23×10^{-3} M at 8.0 and 20.0 °C respectively, at $\mu = 1.0$ M, H_2O 100%. For the water/alcohol mixtures the following values were adopted: Alcohol 20% v/v: $K_h = 1.3 \times 10^{-3}$ (8.0°) and 2.6×10^{-3} (20.0 °C); 30% v/v: 1.8×10^{-3} and 3.7×10^{-3}; 36% v/v : 2.25×10^{-3} and 4.6×10^{-3} M respectively. Wada and Kobaiashi reported data for K_h at different water–methanol mixtures[10] at 25.0 °C and $\mu = 1.0$ M. The corresponding log K_h values are linear as a function of alcoholic percent up to 60% v/v; therefore the desired values were obtained by interpolation. The same ΔH_h (10.2 kcal mol^{-1} at $\mu = 1.0$ M)[9] was assumed to hold for water/alcoholic mixtures in order to obtain the values at 8.0° and 20.0°C. The values for 30% MeOH v/v mixtures were used for 30% *n*PrOH v/v mixtures.

The following *p*K's determined at $\mu = 1.0$ M were obtained from the literature[11] for the ligands: L(+)–tartaric acid, $pK_1 = 2.60$, $pK_2 = 3.77$; citric acid: $pK_1 = 2.52$, $pK_2 = 3.81$.

Apparatus. – UV-visible spectra were recorded with a Perkin–Elmer EPS 3T spectrophotometer.

The kinetic experiments were carried out with a Durrum Gibson stopped-flow spectrophotometer following the procedure previously described. PH measurements were performed on a Ionalyzer Orion Research mod. 801 digital pH meter equipped with calomel (NaCl bridge) and glass electrodes.

RESULTS AND DISCUSSION

Equilibrium Measurements. – Complex formation of Fe(III) with ligands bearing polyaminocarboxylic,[12] α-hydroxycarboxylic[1] and orthodiphenolic[13] moieties give rise to chelated complexes with 1 : 1 metal to ligand ratios, at $pH \leqslant 2$, even in the presence of a large excess of ligand.

By mixing Fe(III) perchlorate (~ 10^{-4} M) with excess tartaric or citric acid ($10^{-3} \div 10^{-2}$ M) at $pH \leqslant 2{,}0$, a strong increase of absorbance is rapidly obtained in the range 350 ÷ 420 nm (both ligands do not absorb in this region). Absorption data obtained after equilibration of the reactants (at 380 nm for tartaric and 390 for citric acid) agreed with the following stoichiometry

$$Fe^{3+}_{aq} + H_4L_{aq} \underset{}{\overset{K_{eq}}{\rightleftharpoons}} FeH_{4-n}L_{aq} + nH^{+}_{aq} \tag{4}$$

Assuming that the complex is the only absorbing species in the reaction mixture (absorption due to the free metal is very low and can be neglected compared to that of the product) the following equations can be derived

$$A = \epsilon_c\, 1\, [FeH_{4-n}L] \tag{5}$$

$$C_{Fe} = [Fe^{3+}] + [FeOH^{2+}] + [FeH_{4-n}L] \tag{6}$$

$$Fe^{3+}_{aq} \rightleftharpoons FeOH^{2+}_{aq} + H^{+}_{aq},\ K_h \tag{7}$$

where A is the absorbance, 1 the light pathway and ϵ_c the molar absorptivity of the complex; Fe^{3+} and $FeOH^{2+}$ are the only important cation species in the present experimental conditions: $[Fe(III)] \leqslant 3 \times 10^{-4}$ M, $pH \leqslant 2.0$. From the equations 5–7:

$$\begin{aligned} C_{Fe}/A &= (1/(\epsilon_c 1) + \{1/(\epsilon_c\, 1\, K_{eq})\}[H^+]^n \\ &\quad (1 + K_h [H^+]^{-1})/[H_4L] \\ &= 1/(\epsilon_c\, 1) + \{1/(\epsilon_c\, 1\, K_{eq})\}\{[H^+]^n \\ &\quad (1 + K_h [H^+]^{-1})/\{(C_L - A/(\epsilon_c 1))\alpha_{H_4L}\}\} \end{aligned} \tag{8}$$

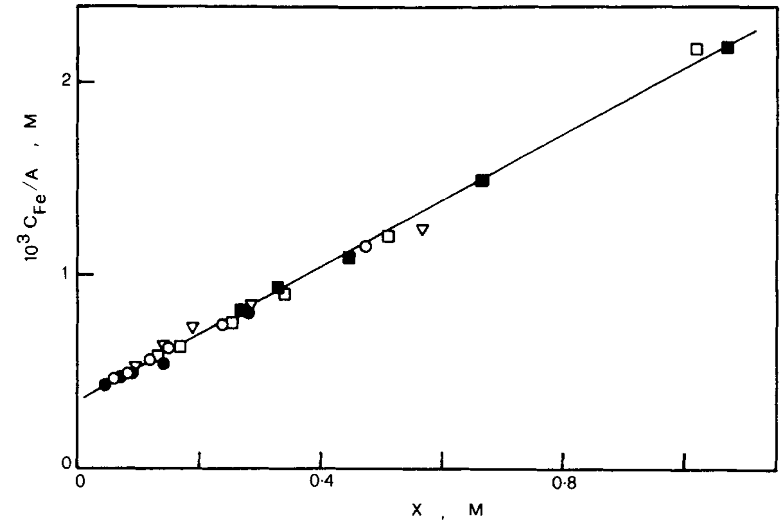

FIGURE 1 Plot of C_{Fe}/A as a function of $[H^+]^2 (1 + K_h[H^+]^{-1}) / \{(C_L - A/(\epsilon l))\alpha_{H_4L}\}$ for the reaction of tartaric acid at 20.0 °C, H_2O 100%. $[H^+]$ as follows: ●, 0.010 M; ▽, 0.015 M; ○, 0.020 M; □, 0.030 M; ■, 0.050 M.

where C_L is the stoichiometric concentration of the ligand and α_{H_4L} is given by

$$\alpha_{H_4L} = [H^+]^3/([H^+]^3 + [H^+]^2K_1 + [H^+]K_1K_2). \qquad (9)$$

The third protolytic step for citric acid can be ruled out in the computation of α_{H_4L} in the investigated conditions. Plots of C_{Fe}/A as a function of $\{[H^+]^n(1 + K_h[H^+]^{-1})/\{(C_L - A/(\epsilon_c l))\alpha_{H_4L}\}\}$ (successive iterations were applied in order to take into account the originally unknown $A/\epsilon_c l$ term) were linear with $n = 2$ for tartaric and $n = 3$ for citric acid; see Figures 1 and 2, as an example.

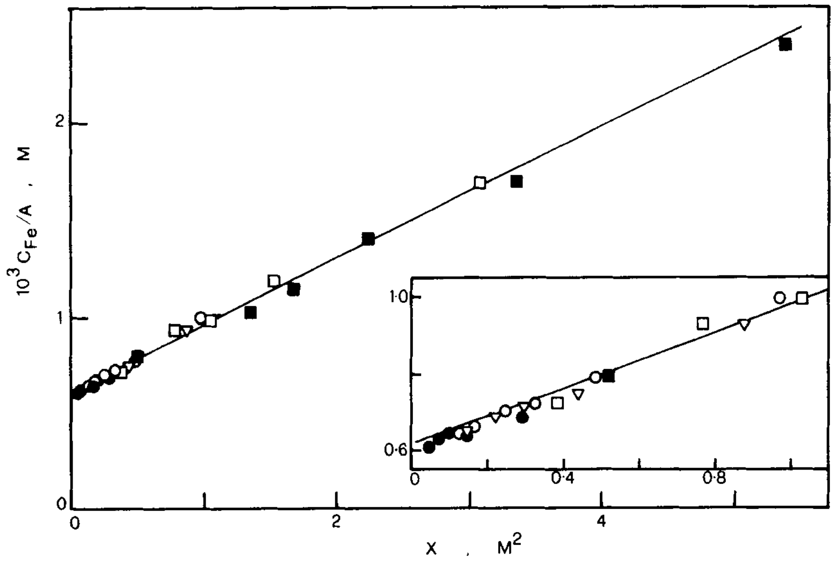

FIGURE 2 Plot of C_{Fe}/A as a function of $[H^+]^3 (1 + K_h[H^+]^{-1})/\{(C_L - A/(\epsilon l))\alpha_{H_4L}\}$ for the reaction of citric acid at 20.0 °C, H_2O 100%. Acidities as for Figure 1.

TABLE I

Equilibrium data for the reactions of Fe(III) with tartaric and citric acid together with the values for other α-hydroxycarboxylic acids[1]

Ligand	Medium	t/°C	10^2 K_{eq}, M	ϵ, M^{-1} cm^{-1}
L(+) Tartaric	H_2O	20.0	21.0	1380 (380 nm)
	H_2O	8.0	18.0	
	MeOH 20%	20.0	23.5	
	MeOH 36%	20.0	24.6	
Citric[a]	H_2O	20.0	1.86	780 (390 nm)
	H_2O	8.0	1.58	
	MeOH 20%	20.0	2.01	
	MeOH 36%	20.0	2.56	
	*n*PrOH 30%	20.0	2.90	
Glycolic	H_2O	20.0	2.3	
DL Lactic	H_2O	20.0	2.6	
DL Malic	H_2O	20.0	8.7	
Benzilic	H_2O	20.0	34	

[a] K_{eq} unit for citric acid: M^2. The error on K_{eq} values is ± 3–5%.

From intercept and gradient of the above plots ϵ_c and K_{eq} could be evaluated in different experimental conditions; the derived parameters are collected in Table I. The good linearities ensure also that for these systems no higher ligand/metal ratios than unity were operating and that two protons are displaced from tartaric and three from citric acid.

In the same conditions Fe^{3+} displaces two protons from the α-OH-COOH moiety (as in the case of glycolic acid)[1]. Tartaric acid has two carboxylic and two α-hydroxy groups whereas citric acid has three carboxylic groups and one α-OH group. In order to clarify the structure of the complexes, i.e. the bonding mode of the ligand, some comparisons and considerations must be made.

In the case of tartaric acid the two linking sites could be i) the two dissociated carboxylic groups, or ii) one carboxylic and the adjacent hydroxy group. Bonding to the two carboxylato groups would lead to a less favourable seven-membered chelation ring but the deprotonation would involve two easily dissociable groups. This behaviour can be modelled by the reaction of Fe(III) with succinic acid. In the latter case the chelation ring would be five-membered but deprotonation would involve an alcoholic group whose acidity is very low. This behaviour could be compared with the ones of other simple α-hydroxycarboxylic acids. As it can be seen in Table I K_{eq} for tartaric acid inserts reasonably well in the series whereas it cannot be compared with the value for succinic acid ($K_{eq} \simeq 5 \times 10^{-3}$ M at $\mu = 1.0$ M).[14]

Therefore it is assumed that tartaric acid coordinates to Fe(III) with full deprotonation of one α-hydroxycarboxylic segment.

This behaviour, even if not generally displayed, resembles the ones of some divalent metal ions such as Cu^{2+},[15] and Ni^{2+},[16] and of UO_2^{2+},[17] and Ce^{4+}[18] which are able to displace the hydroxy alcoholic proton of tartaric or citric acid. No simple comparison criteria can be advanced for citric acid but equilibrium measurements performed with tricarballylic acid (a triprotic acid which corresponds to citric acid with an -H instead of the alcoholic -OH group) showed that, at the same ionic strength, temperature and acidity the spectrum of Fe(III) perchlorate does not change significantly after addition of this tricarboxylic ligand in such concentrations that, with citric acid, the metal would have been brought to nearly complete complexation. Thus also for citric acid coordination through a deprotonated hydroxy group and two carboxylato groups can be proposed. This is not only in agreement with the findings concerning tartaric acid but also previous observations.[15,16]

It must be pointed out that one or more of the displaced protons could arise from dissociation of water molecules coordinated to the metal centre: i.e. the formation of a monodentate hydroxo complex for tartaric and a bidentate hydroxo complex for citric acid (one proton from H_2O coordinated to the metal and one from a -COOH group of tartaric or two protons from the -COOH groups of citric acid); this possibility however can be ruled out, in fact if we examine the complex Fe(III)-acetate (which can be the model for Fe(III)-tartaric acid) where a monodentate is the only possible complex, the tendency to form the corresponding hydroxo species is very low and occurs at $pH > 5$,[19] therefore it seems impossible that in the case of tartaric complex the metal centre could have an acidity of 3 orders of magnitude higher, i.e. hydroxo species formed in a pH range lower than 2. In addition this seems unlikely, in fact it would mean that Fe(III) hydrolyzes more easily if bonded to a ligand rather than as a free aquoin ($pK_h = 2.8$ at 25 °, $\mu = 1.0$ M, H_2O 100%).[9]

Reaction Kinetics. – The kinetics of complex formation were followed under the same experimental conditions. By following the absorbance increase in the presence of a large excess of ligand, pseudo-first order conditions were fulfilled and plots of $\ln(A_{eq} - A_t)$ vs. time were linear up to 90% reaction progress (A_{eq} and A_t represent the absorbance at equilibrium and at time t). In the case of tartaric acid the following reaction sequence can be written

$$Fe^{3+}_{aq} + H_4L \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} FeH_2L^+ + 2H^+ \tag{10}$$

$$FeOH^{2+}_{aq} + H_4L \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} FeH_2L^+ + H^+ + H_2O \tag{11}$$

$$Fe^{3+}_{aq} + H_3L^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} FeH_2L^+ + H^+ \tag{12}$$

$$FeOH^{2+}_{aq} + H_3L^- \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} FeH_2L^+ + H_2O \tag{13}$$

Fe^{3+} and $FeOH^{2+}$ are the only important cation species in the present experimental conditions and H_2L^{2-} ligand species is not taken into account because its contribution would give a dependence of the rate on acidity of the type $[H^+]^{-3}$ with the hydrolyzed metal species which has not been observed (see below). From the sequence it follows:

$$d[X]/dt = \{k_1 + (k_2K_h + k_3K_1)[H^+]^{-1} + k_4[H^+]^{-2}K_hK_1\}\left\{\frac{[H_4L]}{1 + K_h[H^+]^{-1}} + \frac{[H^+]^2}{K_{eq}}\right\} \times ([X]_{eq} - [X]) \tag{14}$$

where X stays for the complex; after integration it is obtained:

$$\ln\{([X]_{eq} - [X]_0)/([X]_{eq} - [X]_t)\} = k_{obsd} \times t \tag{15}$$

where k_{obsd} is the pseudo-first order rate constant obtained from the plots mentioned above which can be written in the form:[1]

$$k_{obsd} = k_f \times C_L + k_r \tag{16}$$

where

$$k_f = \{k_1 + (k_2K_h + k_3K_1)[H^+]^{-1} + k_4K_hK_1[H^+]^{-2}\}\frac{\alpha_{H_4L}}{1 + K_h[H^+]^{-1}} \tag{17}$$

and

$$k_r = k_{-1}[H^+]^2 + (k_{-2} + k_{-3})[H^+] + k_{-4} \tag{18}$$

Plots of k_{obsd} as a function of C_L were linear, at constant acidity (see Figure 3 as an example), and enabled the evaluation of k_f and k_r. Table II collects these parameters for different conditions.

Figure 4 shows as an example plots of $k_f(1 + K_h[H^+]^{-1})[H^+]/\alpha_{H_4L}$ as a function of $[H^+]^{-1}$. The linearity points out the presence of a term dependent on $[H^+]^{-1}$ (intercept) and a term $[H^+]^{-2}$ dependent (gradient), and suggests that the k_1 term in eq. (17) is negligible. From these plots the values of $(k_2K_h + k_3K_1)$ and $k_4K_hK_1$ could be evaluated. Figure 5 shows the dependence of the reverse reactions, for tartaric acid at 8.0 and 20.0 °C

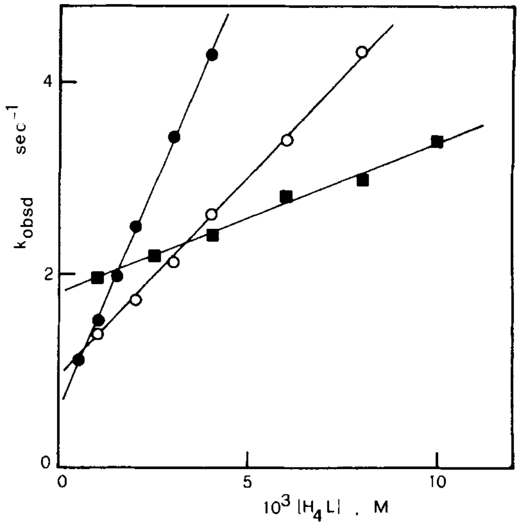

FIGURE 3 Variation of k_{obsd} as a function of the ligand concentration, for the reaction of tartaric acid at 20.0 °C, H_2O 100%. $[H^+]$ as follows: ●, 0.010 M; ○, 0.020 M; ■, 0.050 M.

TABLE II

Forward, k_f (M^{-1} sec^{-1}), and reverse, k_r (sec^{-1}), observed rate constants, see eqq. (16)–(19), for the investigated reactions in different experimental conditions

			$[HClO_4]$, M				
			0.010	0.015	0.020	0.030	0.050
L(+) Tartaric Acid							
H_2O	20.0 °C	k_f	938	570	420	248	143
		k_r	0.625	0.760	0.900	1.27	1.82
H_2O	8.0°	k_f	200	133	97	62	35
		k_r	0.22	0.25	0.30	0.41	0.60
MeOH 20%	20.0°	k_f	1034	610	470	280	175
		k_r	0.67	0.80	1.00	1.36	1.96
MeOH 20%	8.0°	k_f	203	123	102	65	40
		k_r	0.28	0.33	0.36	0.44	0.55
MeOH 36%	20.0°	k_f	1560	900	670	400	210
		k_r	0.55	0.76	0.94	1.33	2.10
MeOH 36%	8.0°	k_f	342	220	140	74	45
		k_r	0.23	0.30	0.40	0.51	0.75
Citric acid							
H_2O	20.0°C	k_f	930	50	355	210	110
H_2O		k_r	0.10	0.165	0.23	0.41	0.85
H_2O	8.0°	k_f	214	122	86	52	31
		k_r	0.040	0.065	0.086	0.148	0.280
MeOH 20%	20.0°	k_f	1160	690	454	270	152
		k_r	0.09	0.165	0.27	0.50	1.00
MeOH 36%	20.0°	k_f	1430	800	568	320	128
		k_r	0.10	0.18	0.30	0.57	1.30
*n*PrOH 30%	20.0°	k_f	1500	850	600	352	180
		k_r	0.08	0.14	0.20	0.35	0.73

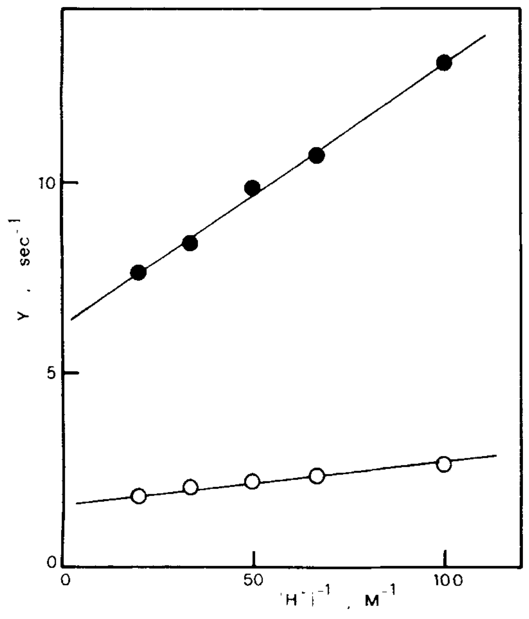

FIGURE 4 Plots of $k_f[H^+](1+K_h[H^+]^{-1})/\alpha_{H_4L}$ as a function of $[H^+]^{-1}$ for the reaction of tartaric acid in H_2O 100%. ●, 20.0 °C; ○, 8.0 °C.

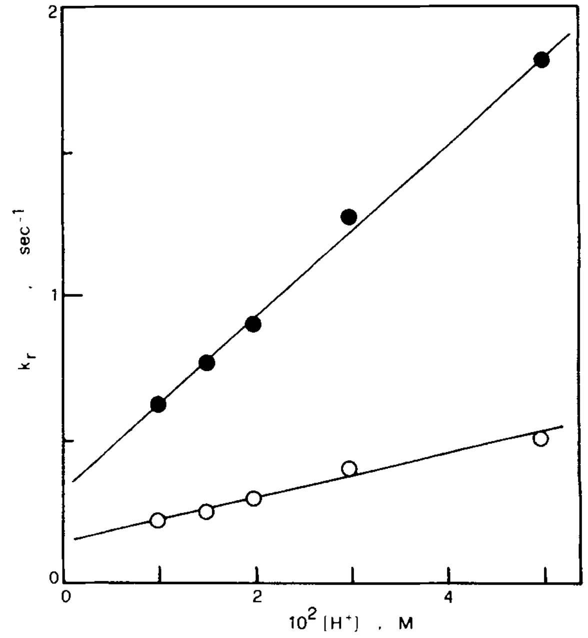

FIGURE 5 Variation of k_r as a function of acidity for the reaction of tartaric acid in H_2O 100%. ●, 20.0 °C; ○, 8.0 °C.

as an example, on acidity; again the linearity of plots of k_r as a function of $[H^+]$ shows that $k_{-1}[H^+]^2$ term in eq. (18) is negligible and from the slope and intercept of such plots $(k_{-2} + k_{-3})$ and k_{-4} could be evaluated, in agreement with the microscopic reversibility principle.

If we take into account the term $k_2K_h + k_3K_1$, since $K_h \simeq K_1$, and since $FeOH^{2+}$ is much more labile than $Fe^{3+}(k_2 \gg k_3)$ (in fact $FeOH^{2+}$ has been always found orders of magnitude more reactive than Fe^{3+})[1,13,21] it must be $k_2K_h \gg k_3K_1$ and therefore forward and reverse contributions can be assigned to reactions (11) and (13).

Table III collects the values of the derived kinetic parameters together with the activation parameters. It is worth to mention that the data in Table III enable the evaluation of the equilibrium constant K_{eq} from kinetic data; in fact it can be obtained, for tartaric acid at 20.0 °C and H_2O 100%. $k_2K_h/k_{-2} = K_{eq} = 0.217$ M and $k_4K_hK_1/k_{-4} = K_{eq} = 0.209$ to be compared with the spectrophotometric value $K_{eq} = 0.210$ M. These values are in very good agreement and give support to the advanced mechanism and stoichiometry.

The derived forward specific rate constants are typical of the investigated metal ion and can be compared with the ones that can be computed theoretically from the water exchange rate (k^*) of $FeOH^{2+}$ [1,4b,22,23] and the precursor ion pair stability constant K_0 on the basis of an SN1 IP mechanism.

In fact, according to the Eigen Tamm model,[4,24] the specific rate constants for complex formation are given by the product of the equilibrium constant K_0 of the outer-sphere complex, in which the metal and ligand are separated by one or more solvent molecules, and the rate of penetration of the ligand into the inner coordination sphere of the metal and this process is determined by the rate of the solvent molecules exchange, k^*, at the metal centre. If it is assumed 5 Å the distance of maximum approach of the ligand to $FeOH^{2+}$ (this is the distance which is admitted by the water molecules of the hydration shell of the metal) K_0 can be computed to be, according to electrostatic models, 0.2 and 2 M respectively[3,25] for the reactions (11) and (13) at 25 °C.

Then it follows $k_2 = K_0k^* = 0.2 \times 2 \times 10^4 = 4 \times 10^3\ M^{-1}\ sec^{-1}$ to be compared with the experimental values 5.1×10^3 and $3.1 \times 10^3\ M^{-1}\ sec^{-1}$ for tartaric and citric acid respectively and $k_4 = K_0k^* = 2 \times 2 \times 10^4 = 4 \times 10^4\ M^{-1}\ sec^{-1}$ to be compared with 2.2×10^4 and $2.6 \times 10^4\ M^{-1}\ sec^{-1}$ respectively.

TABLE III

Kinetic parameters for the investigated reactions[a]

Ligand	Medium	t/°C	$10^{-3}\ k_2$ $M^{-1}\ sec^{-1}$	$\Delta H^{\neq}(k_2)$ kcal mol^{-1}	$\Delta S^{\neq}(k_2)$ cal $mol^{-1}\ K^{-1}$	$10^{-4}\ k_4$ $M^{-1}\ sec^{-1}$	$\Delta H^{\neq}(k_4)$ kcal mol^{-1}	$\Delta S^{\neq}(k_4)$ cal $mol^{-1}\ K^{-1}$	k_{-2}[b] $M^{-1}\ sec^{-1}$	k_{-4}[c] sec^{-1}
Tartaric acid										
	H_2O	20.0	5.1	7.6	−16	2.2	15.1	13	29	0.33
	H_2O	8.0	2.8			0.70			9.4	0.12
	MeOH 20%	20.0	3.0	8.9	−12	1.2	19.4	26	32	0.35
	MeOH 20%	8.0	1.5			0.28			7.0	0.20
	MeOH 36%	20.0	1.7	9.7	−11	1.7	13.2	6	40	0.12
	MeOH 36%	8.0	0.8			0.62			13.2	0.10
Citric acid										
	H_2O	20.0	3.1	5.4	−24	2.6	5.4	−24	180	8.0
	H_2O	8.0	2.0			1.5			44	3.5
	MeOH 20%	20.0	2.2			1.7			300	6.0
	MeOH 36%	20.0	0.87			1.6			400	6.0
	*n*PrOH 30%	20.0	1.7			1.8			150	7.0

[a] The error in the values of the reported forward and reverse rate constants is ± 6–8%; the uncertainty in the values of $\Delta H^{\neq}$ is ± 1 kcal mol^{-1} and of $\Delta S^{\neq}$ is ± 3 cal $mol^{-1}\ K^{-1}$.

[b] The unit for k_{-2} for citric acid is $M^{-2}\ sec^{-1}$.

[c] The unit for k_{-4} for citric acid is $M^{-1}\ sec^{-1}$.

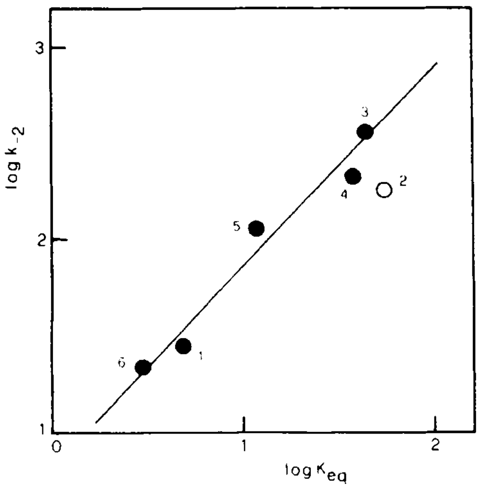

FIGURE 6 Variation of log k_{-2} as a function of log K_{eq}, 20.0 °C, H_2O 100%. Ligands: 1, tartaric; 2, citric; 3, glycolic; 4, lactic; 5, malic; 6, benzilic acid. For ligands 3–6, see ref. (1).

If forward rates are independent of the ligand, the reverse reactions will be affected by the stability of the complexes i.e. the more stable the complex the slower the reverse process must be.[1,26] Figure 6 shows a plot of log K_{eq} as a function of log k_{-2} for the previously investigated simple α-OH acids; as it can be seen the value for tartaric acids fits well confirming again that in the investigated *p*H range tartaric acid behaves in respect to Fe(III) as a simple hydroxyacid.

In the case of citric acid the same reaction sequence as in (10) (13) can be written with formation of FeHL complex and one additional proton for each pathway. Also the expressions (15), (16) and (17) are still valid, whereas the overall reverse reaction rate is of the form:

$$k_r = k_{-1}[H^+]^3 + (k_{-2} + k_{-3})[H^+]^2 + k_{-4}[H^+] \qquad (19)$$

The same dependence of k_f on acidity, as for tartaric acid, has been observed (see Table II), from which, under the same assumptions, the values of k_2 and k_4 could be evaluated (see Table III).

For the reverse reactions, the microscopic reversibility principle predicts a combined $[H^+]^2$ (reaction (11)) and $[H^+]$ (reaction (13)). Plots of $k_r[H^+]^{-1}$ against $[H^+]$ were linear in agreement with this expectation.

Also for citric acid the equilibrium constant K_{eq} can be derived kinetically for each path; at 20.0 °C and H_2O 100% the following values were obtained: for path (11) $K_{eq} = 2.1 \times 10^{-2}$ and for path (13) 1.2×10^{-2} M^2 to be compared with the spectrophotometric value 1.86×10^{-2} M^2. There is some scattering in the equilibrium quotients that can be evaluated kinetically from both paths and this is due mainly to the higher uncertainty that pertains to the kinetic measurements. However if a mean value is computed between the data of each path, it is obtained for citric acid: $K_{eq} = 1.7 \times 10^{-2}$ M^2, 20.0 °C H_2O 100%; 1.6×10^{-2} 8.0 °C H_2O 100%; 2.1×10^{-2}, 20.0 °C MeOH 20%; 2.4×10^{-2}, 20.0 °C MeOH 36%; 3.4×10^{-2}, 20.0 °C *n*PrOH 30%. This trend agrees with a higher stabilization of the complex with the increasing alcohol content, i.e. with the lowering of the dielectric constant of the medium.

Turning now to the effect of the solvent composition on the reaction rates, both K_0 and k^* can be affected by the medium variation. K_0 value will be mainly altered by electrostatic effects: on one side by the variation of the dielectric constant of the medium, and on the other by the variation of the solvent sheath thickness between metal and ligand during the outer-sphere equilibrium state. The variation of K_0 will be affected in opposite ways by these two actions: the increase of alcohol content will produce a reduction of the dielectric constant and a parallel increase of association between the reactants, but substitution H_2O/CH_3OH should bring to an increased metal–ligand distance. Also k^* is affected by the variation of solvent composition. In fact for several bivalent metal ions k^* is more than one order of magnitude lower in CH_3OH than in water.[27] A smooth variation in the same direction is displayed by the rate of reaction between Ni^{++} and 2,2′-bipyridyl in H_2O–CH_3OH mixtures.[28] The same kind of variation is expected for $FeOH^{++}$ which can be regarded, from a kinetic point of view, as a bivalent metal ion.[1] The present experimental findings show a lowering of k_2 and a constancy of k_4 values with increasing the organic component. Therefore the specific solvation effects (k^* decrease with increasing alcohol content) result, at least, equal (i.e. for reaction 13) or more important (as in the case of reaction 11) then the electrostatic ones (increase of K_0).

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