

Kinetics of Complex Formation between Some Dicarboxylic Acids and Iron(III) in Aqueous Solution

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The dissociation constants of dimethylmalonic, diethylmalonic, cyclopropane-1,1-dicarboxylic and cyclopentane-1,1-dicarboxylic acids, and the stability constants of the corresponding iron(III) monochelates have been estimated at 25 °C and ionic strength 0.50M. The kinetics of complex formation have been studied by the temperature-jump method over the acidity range 0.04–0.48M. The kinetic data indicate that the reactions of $Fe(H_2O)_5OH^{2+}$ with the neutral and monoanionic ligands contribute significantly to the complex formation. The similar rate constants found for all the reactions involving the neutral ligands suggest the occurrence of a dissociative mechanism. As to the reactions with monoanionic ligands, appreciably smaller rates are observed in the case of diethylmalonate and cyclopropane-1,1-dicarboxylate monoanions. Two possible mechanisms are proposed.

Introduction

In the last years increasing attention has been paid to the kinetics and mechanism of formation of iron(III) complexes in aqueous solution and quite a large amount of kinetic data is now available [1–13]. The majority of these data, however, concern a variety of monodentate ligands, whereas those regarding chelating agents are relatively few. Systematic kinetic studies involving the simpler chelating ligands (*i.e.*, bidentate ones) appear to be of interest in an attempt to ascertain in the case of iron(III) monochelate formation the occurrence of the “sterically controlled substitution” [14] or of the “internal conjugate base” (ICB) mechanism [15] proposed for some divalent transition metal chelate formation.

As an extension of a previous kinetic investigation [1], we have now studied by the temperature-jump method the kinetics of the complexation reactions of iron(III) with four disubstituted malonic acids [*i.e.*,

dimethylmalonic (DMMA), diethylmalonic (DEMA), cyclopropane-1,1-dicarboxylic (CPRDA) and cyclopentane-1,1-dicarboxylic (CPEDA) acids] under the experimental conditions of temperature (25 °C) and ionic strength (0.50M) used earlier. The present kinetic data together with those previously obtained [1] using other malonic acid derivatives allow us to study the influence of the ligand basicity and of the steric hindrance of the substituent groups on the mechanism of iron(III) monochelate formation. The first and second dissociation constants (K_1 and K_2) of the ligands considered and the stability constants (K_C) of the corresponding iron(III) monocomplexes have been also estimated.

Experimental

Diethylmalonic, cyclopropane-1,1-dicarboxylic and cyclopentane-1,1-dicarboxylic acids were prepared [1] by basic hydrolysis of their diethyl esters (Fluka). The products obtained and the commercial (Fluka) dimethylmalonic acid were purified as described elsewhere [1]. The solutions of the ligands, sodium perchlorate (supporting electrolyte) and iron(III) perchlorate were prepared as reported earlier [1].

Potentiometric titrations were carried out to determine the dissociation constants (K_1 and K_2) of the dicarboxylic acids at 25 °C and ionic strength 0.50M with the experimental procedure previously described [1]. Noyes' method [16] was used to estimate the K_1 and K_2 values for dimethylmalonic and cyclopentane-1,1-dicarboxylic acids ($pK_2 - pK_1 < 2.7$), whereas for diethylmalonic and cyclopropane-1,1-dicarboxylic acids ($pK_2 - pK_1 > 2.7$) the procedure described by Albert and Serjeant was followed [16]. The equilibrium constants (K_C) for the formation of the iron(III) monocomplexes were obtained by the kinetic method previously adopted [1] (see below).

The temperature-jump experiments were performed with the same technique as employed before [1]. The observed relaxation times are affected by a maximum uncertainty of *ca.* ± 8%.

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TABLE I. Dissociation Constants of Dicarboxylic Acids and Stability Constants of the Corresponding Iron(III) Monochelates ($t = 25.0\text{ }^{\circ}\text{C}$, $\mu = 0.50M$).

Acid	$10^3 K_1$ (M)	$10^6 K_2$ (M)	$10^{-7} K_C$ (M^{-1})	$\Delta pK =$ $= pK_2 - pK_1$
Dimethylmalonic	1.45 ± 0.06	4.2 ± 0.1	1.43 ± 0.08	2.54
Diethylmalonic	14.1 ± 0.6	0.240 ± 0.005	7.3 ± 0.4	4.77
CPRDA ^a	32.4 ± 0.8	0.126 ± 0.003	55 ± 3	5.41
CPEDA ^b	1.10 ± 0.03	3.24 ± 0.08	4.2 ± 0.3	2.53
Malonic ^c	2.4	9.3	3.7	2.41
Methylmalonic ^c	1.5	7.2	3.6	2.32
n-Butylmalonic ^c	1.7	6.3	2.0	2.43
Benzylmalonic ^c	2.5	9.6	1.8	2.42
CBUDA ^{c,d}	1.38	6.0	2.9	2.36

^aCyclopropane-1,1-dicarboxylic acid. ^bCyclopentane-1,1-dicarboxylic acid. ^cRef. 1. ^dCyclobutane-1,1-dicarboxylic acid.

Results and Discussion

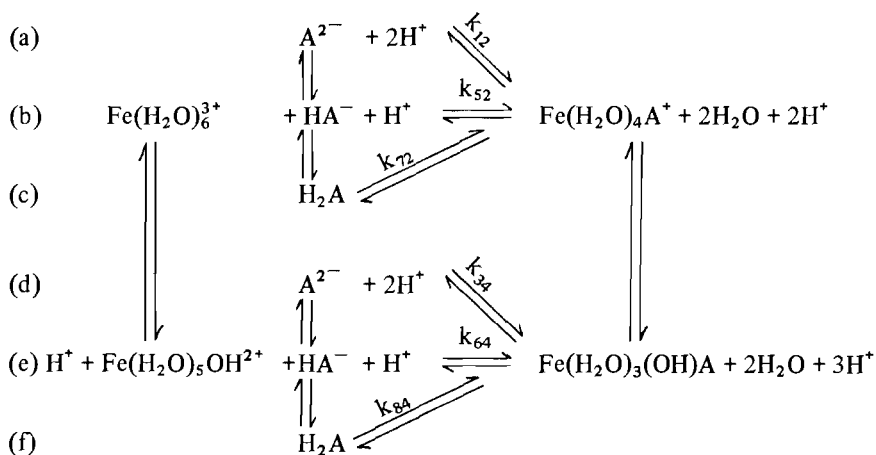
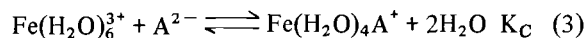
The dissociation constants of the dicarboxylic acids estimated in this work are given in Table I together with those previously obtained [1]. A comparison of the present data with those reported in the literature is not possible because of the different experimental conditions used. Our K_1 and K_2 values are however always larger than the corresponding values obtained [17–19] at $25\text{ }^{\circ}\text{C}$ and ionic strength $0.10M$, as expected on the basis of the ionic strength effects [19, 20].

The present kinetic results are found to conform to the reaction scheme proposed for the malonic acid derivatives examined earlier [1]. According to this Scheme (see below) six reactions may contribute, in the most general case, to the formation of the iron(III) monochelates, *i.e.*, the reactions of the $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ and $\text{Fe}(\text{H}_2\text{O})_5\text{OH}^{2+}$ ions with the neutral, monoanionic and dianionic forms of the ligands (A^{2-} represents the dianionic form of the dicarboxylic

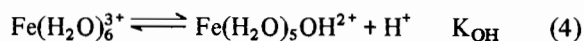
acids). Under the experimental conditions used, the derived equation [1] for the relaxation time τ is given by the six-term expression (1), where C [equation (2); square brackets indicate equilibrium concentrations], α , β , γ are quantities depending on the equilibrium concentrations of the predominant chemical species present in solutions, and K_C and K_{OH} ($= 1.87 \times 10^{-3}M$ [1]) represent the equilibrium constants for the reactions (3) and (4).

$$\frac{1}{\tau C} = k_{\text{obs}} = \left(k_{12} + \frac{k_{64} K_{\text{OH}}}{K_2}\right) + \left(\frac{k_{52}}{K_2} + \frac{k_{84} K_{\text{OH}}}{K_1 K_2}\right) [\text{H}^+] + \frac{k_{72} [\text{H}^+]^2}{K_1 K_2} + \frac{k_{34} K_{\text{OH}}}{[\text{H}^+]}$$
 (1)

$$C = \frac{[\text{Fe}^{3+}]}{1 + \beta + \gamma} + \frac{[\text{A}^{2-}]}{1 + \alpha} + \frac{1}{K_C}$$
 (2)



Reaction Scheme



When the hydrogen-ion concentration is maintained constant, equation (1) can be rewritten as shown in (5) and the stability constant K_C can be then estimated [1] from the slope: intercept ratio obtained by plotting $1/\tau$ against the quantity $\{[\text{Fe}^{3+}]/$

$$\frac{1}{\tau} = \frac{k_{\text{obs}}}{K_C} + k_{\text{obs}} \left(\frac{[\text{Fe}^{3+}]}{1 + \beta + \gamma} + \frac{[\text{A}^{2-}]}{1 + \alpha} \right) \quad (5)$$

$(1 + \beta + \gamma) + [\text{A}^{2-}]/(1 + \alpha)$. Kinetic data obtained at constant acidity ($[\text{H}^+] = 0.100M$) and at various total concentrations of iron(III) perchlorate and dicarboxylic acids are assembled in Table II. Since the equilibrium concentrations were unknown, the evaluation of the stability constant K_C was made by means of an iterative program run on an IBM 370/145 computer using an arbitrary initial K_C value. In any case the output final K_C value was independent of the initial choice. This program was also used to re-

TABLE II. Kinetic Data at Constant Acidity ($[\text{H}^+] = 0.100M$, $t = 25.0^\circ\text{C}$, $\mu = 0.50M$).

$10^3(\text{Fe})_{\text{T}}^{\text{a}}$ (M)	$10^3(\text{H}_2\text{A})_{\text{T}}^{\text{a}}$ (M)	$10^9 \left(\frac{[\text{Fe}^{3+}]}{1 + \beta + \gamma} + \frac{[\text{A}^{2-}]}{1 + \alpha} \right)$ (M)	10τ (sec)	$10^3(\text{Fe})_{\text{T}}^{\text{a}}$ (M)	$10^3(\text{H}_2\text{A})_{\text{T}}^{\text{a}}$ (M)	$10^9 \left(\frac{[\text{Fe}^{3+}]}{1 + \beta + \gamma} + \frac{[\text{A}^{2-}]}{1 + \alpha} \right)$ (M)	10τ (sec)
Dimethylmalonic acid				Cyclopropane-1,1-dicarboxylic acid			
3.00	1.00	2.39	1.10	1.00	1.50	0.657	5.3
3.00	3.00	3.64	1.09	1.50	1.50	0.765	5.0
4.00	3.00	4.27	1.00	1.50	2.00	0.878	4.8
4.00	4.00	4.90	1.06	2.00	2.00	0.980	4.2
5.00	5.00	6.18	0.98	2.00	3.00	1.20	4.3
6.00	6.00	7.49	0.97	3.00	3.00	1.37	4.1
4.00	10.0	8.70	0.95	3.00	3.50	1.47	3.9
8.00	6.00	8.80	0.92	3.00	4.00	1.57	3.6
6.00	10.0	10.1	0.92	4.00	4.00	1.73	3.5
6.00	12.0	11.4	0.88	4.00	6.00	2.10	3.2
6.00	14.0	12.7	0.93	4.00	8.00	2.53	2.9
6.00	18.0	15.3	0.88	5.00	8.00	2.60	2.9
8.00	16.0	15.5	0.91	5.00	9.00	2.81	2.7
8.00	24.0	20.8	0.84	5.00	10.0	3.03	2.6
12.0	24.0	24.0	0.82	6.00	10.0	3.08	2.6
9.00	30.0	25.6	0.80	6.00	11.0	3.29	2.5
Diethylmalonic acid				Cyclopentane-1,1-dicarboxylic acid			
1.50	2.00	1.01	2.42	2.00	2.50	1.57	1.08
2.00	2.00	1.16	2.44	3.00	3.00	2.11	1.03
2.00	3.00	1.44	2.37	3.00	4.00	2.46	0.98
2.50	3.00	1.59	2.45	3.00	6.00	3.17	1.02
3.00	3.00	1.73	2.39	4.00	6.00	3.53	0.96
3.00	4.00	2.01	3.33	4.00	8.00	4.25	0.95
4.00	4.00	2.30	2.14	5.00	7.00	4.25	0.98
4.00	5.00	2.58	2.30	5.00	8.00	4.61	0.91
4.00	6.00	2.87	2.29	5.00	9.00	4.97	0.99
5.00	8.00	3.71	1.98	5.00	10.0	5.33	0.91
5.00	8.00	3.71	2.18	6.00	10.0	5.70	0.90
5.00	10.0	4.28	2.05	6.00	12.0	6.42	0.89
6.00	12.0	5.11	1.91	6.00	14.0	7.14	0.86
7.00	14.0	5.95	1.76	7.00	15.0	7.89	0.81
7.00	16.0	6.51	1.70	7.00	17.0	8.61	0.80
8.00	16.0	6.77	1.61	8.00	16.0	8.63	0.76
7.00	18.0	7.07	1.88	8.00	18.0	9.36	0.85
7.00	20.0	7.63	1.72	7.00	20.0	9.69	0.79
7.00	21.0	7.92	1.72	8.00	20.0	10.1	0.77
8.00	21.0	8.18	1.69	7.00	22.0	10.4	0.80
7.00	22.0	8.20	1.64	7.00	25.0	11.5	0.79
8.00	24.0	9.02	1.64				

^aTotal molar concentration.

evaluate the stability constants for the iron(III) systems previously [1] studied, yielding the same K_C values already reported (*cf.* Table I). The stability constants estimated in this work together with the corresponding standard deviations are given in Table I, whereas the final values of the quantity $\{[\text{Fe}^{3+}]/(1 + \beta + \gamma) + [\text{A}^{2-}]/(1 + \alpha)\}$ are in Table II. It should be noted that di-n-butylmalonic and cyclohexane-1,1-dicarboxylic acids were also used as complexing ligands. However, owing to the observed small variation of the relaxation time with the total concentrations of the ligands and iron(III) perchlorate, K_C values with a large uncertainty were obtained and the kinetic measurements were thus discontinued.

It can be seen from Table I that the stability of the iron(III) monomalonate complex decreases when an alkyl group is introduced in the molecule of the malonate anion. The effect of adding two methyl groups is to cause a further decrease in the chelate stability, but the diethyl substitution results in a large increase of the stability which overcomes that of the unsubstituted malonate ion. As to the alicyclic dicarboxylate anions, the iron(III) cyclopropane-1,1-dicarboxylate complex shows a higher stability than all the other complexes examined. Similar stability trends were also observed [17–19, 21] for the corresponding complexes of nickel, cobalt, copper, zinc and lutetium, even though these complexes

TABLE III. Kinetic Data for the Formation of Iron(III) Monochelates with Dicarboxylic Acids ($t = 25.0\text{ }^\circ\text{C}$, $\mu = 0.50M$).

$10^3(\text{Fe})_T^a$ (M)	$10^3(\text{H}_2\text{A})_T^a$ (M)	$10^3[\text{H}^+]$ (M)	10^9C (M)	10τ (sec)	$10^3(\text{Fe})_T^a$ (M)	$10^3(\text{H}_2\text{A})_T^a$ (M)	$10^3[\text{H}^+]$ (M)	10^9C (M)	10τ (sec)
Dimethylmalonic acid					Cyclopropane-1,1-dicarboxylic acid				
2.00	2.00	41.4	84.6	1.44	2.00	2.00	38.6	4.97	3.6
2.00	4.00	73.6	78.1	1.09	2.00	3.00	53.3	4.50	3.8
4.00	7.00	154	74.3	0.78	3.00	5.00	84.6	4.03	3.5
3.00	6.00	194	72.9	0.60	3.00	4.00	141	2.76	4.8
4.00	8.00	206	73.2	0.65	3.00	6.00	158	2.82	3.8
3.00	6.00	242	72.4	0.54	4.00	6.00	213	2.48	3.8
4.00	7.00	287	72.3	0.47	4.00	7.00	259	2.34	3.7
5.00	10.0	301	72.5	0.53	4.00	7.00	281	2.27	4.2
5.00	5.00	345	72.0	0.39	4.00	8.00	322	2.20	3.7
4.00	10.0	383	72.0	0.45	5.00	8.00	379	2.12	3.3
5.00	8.00	388	72.0	0.42	5.00	10.0	388	2.16	3.2
5.00	10.0	401	72.0	0.47	5.00	10.0	425	2.10	3.2
					6.00	12.0	483	2.09	2.9
Diethylmalonic acid					Cyclopentane-1,1-dicarboxylic acid				
2.00	2.00	40.4	19.0	2.84	2.00	2.00	40.4	31.5	1.54
2.50	3.00	42.3	20.3	2.54	2.00	3.00	45.4	31.5	1.82
2.00	4.00	51.5	19.0	2.40	2.50	4.00	49.2	32.4	1.34
3.00	5.00	79.8	17.1	2.42	2.50	4.00	54.5	31.0	1.63
4.00	6.00	127	15.6	2.50	2.00	4.00	78.9	27.1	1.06
4.00	7.00	133	15.6	2.06	3.00	5.00	131	25.5	1.11
3.00	6.00	149	15.0	2.03	3.00	5.00	141	25.3	0.87
4.00	7.00	175	14.8	2.16	3.00	6.00	147	25.3	0.79
4.00	7.00	177	14.8	1.73	3.00	6.00	194	24.7	0.68
4.00	7.00	203	14.6	1.67	4.00	7.00	228	24.6	0.70
3.00	8.00	233	14.4	1.66	4.00	8.00	250	24.5	0.55
4.00	7.00	244	14.3	1.86	4.00	8.00	294	24.3	0.57
4.00	8.00	250	14.3	1.45	5.00	8.00	338	24.2	0.48
4.00	8.00	268	14.2	1.72	5.00	10.0	388	24.2	0.44
4.00	8.00	287	14.2	1.73					
4.00	9.00	326	14.1	1.56					
5.00	9.00	362	14.1	1.23					
5.00	9.00	388	14.0	1.14					
5.00	8.00	397	14.0	1.18					
5.00	9.00	406	14.0	1.39					
5.00	10.0	425	14.0	1.37					

^aTotal molar concentration.

exhibit much smaller K_C values. The observed effects of the structure and basicity of the ligands on the stability of the iron(III) complexes may be explained as before [17–19] in the case of the other metal chelates.

The known equilibrium constants allow us now to study the formation kinetics at varying acidities (Table III). According to equation (1), the linear dependence of k_{obs} on the hydrogen-ion concentration (see Figure 1) observed for all the ligands examined indicates that the terms containing $[H^+]^2$ and $1/[H^+]$ do not contribute significantly to the overall rate. The least-squares analysis of the data gives the values of $(k_{12} + k_{64}K_{OH}/K_2)$ and $(k_{52}/K_2 + k_{84}K_{OH}/K_1K_2)$ collected in Table IV, where the corresponding values previously obtained [1] for other dicarboxylic acids are also reported.

Since the reactions (a) and (e) cannot be kinetically distinguished, an indirect approach has to be used to establish the predominant pathway leading to the chelate formation as made in earlier studies [1–13]. If the values of $(k_{12} + k_{64}K_{OH}/K_2)$ were attributed to k_{12} , the reaction (a) would appear to be unreasonably faster than the analogous reactions involving charged and uncharged [1, 2] ligands (rate constants $\leq ca. 6 \times 10^3 M^{-1} sec^{-1}$ at 22–25 °C and $\mu = 0.1$ – $2.0M$). If, instead, the rate constants k_{64} are estimated by considering $k_{12} \ll k_{64}K_{OH}/K_2$, then it is seen that they are similar to those found for the reactions of $Fe(H_2O)_5OH^{2+}$ and various univalent ligands [1, 2, 4, 5, 11, 12] $[(0.9$ – $4) \times 10^4 M^{-1} sec^{-1}$ at 20–25 °C and $\mu = 0.1$ – $1.7M$ for Cl^- , Br^- , NCS^- , $HCrO_4^-$, $CH_2ClCO_2^-$, $HO_2CCO_2^-$; $(0.9$ – $16) \times 10^4 M^{-1} sec^{-1}$ at $\mu = 0.5$ – $1.0M$ for monoanions of substituted malonic acids, monoanions of salicylic, iminodiacetic, nitrilotriacetic, ethylenediaminetetra-acetic, diethylenetriaminepenta-acetic acids, dianion of sulfosalicylic acid (this dianion acts as a univalent

ligand [4]). Therefore it is reasonable to deduce that only the reaction (e) involving the reacting species $Fe(H_2O)_5OH^{2+}$ and HA^- contributes significantly to the chelate formation.

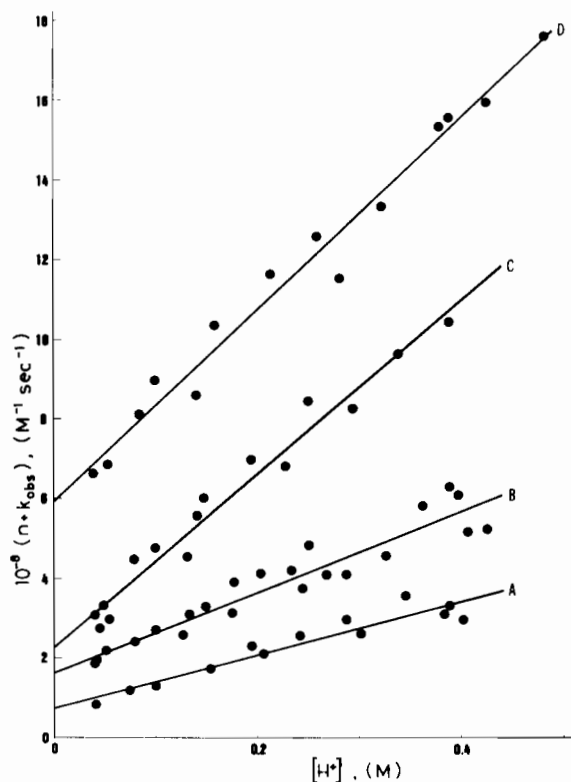


Figure 1. Plots of k_{obs} against the hydrogen-ion concentration; A, dimethylmalonic acid ($n=0$); B, diethylmalonic acid ($n=0$); C, cyclopentane-1,1-dicarboxylic acid ($n=1$); D, cyclopropane-1,1-dicarboxylic acid ($n=1$). The lines are the least-squares fits. The points at $[H^+] = 0.100M$ are the averages of the k_{obs} ($=1/\tau C$) values estimated by the data of Table II and the stability constants K_C (Table I).

TABLE IV. Rate Constants ($M^{-1} sec^{-1}$) for the Formation of Iron(III) Monochelates with Dicarboxylic Acids ($t = 25.0$ °C, $\mu = 0.50M$).

Acid	$10^{-7} \left(k_{12} + \frac{k_{64}K_{OH}}{K_2} \right)^a$	$10^{-8} \left(\frac{k_{52}}{K_2} + \frac{k_{84}K_{OH}}{K_1K_2} \right)$	$10^{-4} k_{64}^b$	$10^{-3} k_{84}^c$
Dimethylmalonic	7.3 ± 1.5	6.7 ± 0.6	16 ± 3	2.2 ± 0.2
Diethylmalonic	17 ± 2	10.0 ± 0.7	2.2 ± 0.3	1.8 ± 0.1
CPRDA ^d	49 ± 3	24 ± 1	3.3 ± 0.2	5.2 ± 0.2
CPEDA ^e	13 ± 2	22 ± 1	22 ± 3	4.2 ± 0.2
Malonic ^f	2.6	5.3	13	6.2
Methylmalonic ^f	3.3	7.5	12	4.3
n-Butylmalonic ^f	3.1	4.6	10	2.6
Benzylmalonic ^f	2.0	4.3	10	5.4
CBUDA ^{f,g}	3.6	7.5	11	3.3

^aThe values reported in this column correspond also to those of k_{12} in the case $k_{12} \gg k_{64}K_{OH}/K_2$. ^bCalculated by assuming $k_{64}K_{OH}/K_2 \gg k_{12}$. ^cCalculated by assuming $k_{84}K_{OH}/K_1K_2 \gg k_{52}/K_2$. ^dCyclopropane-1,1-dicarboxylic acid. ^eCyclopentane-1,1-dicarboxylic acid. ^fRef. 1. ^gCyclobutane-1,1-dicarboxylic acid.

It can be seen from Table IV that in the case of DMMA and CPEDA the k_{64} values are close to those obtained before for malonic acid and its derivatives, whereas the corresponding values for DEMA and CPRDA are appreciably smaller. The lower reaction rates in the latter cases cannot be ascribed to the "sterically controlled substitution" [14] because higher rates are observed with CBUDA and CPEDA which exhibit larger steric hindrances and greater difficulties in closing the chelate ring than the cyclopropane derivative.

Two possible explanations can be advanced to account for the observed different rates in the series of dicarboxylic acids so far examined.

The first explanation is based on the assumption that the reactions involving all the monoanionic ligands, except for the monoanions of DEMA and CPRDA, occur by a "normal substitution" mechanism [1, 2] and, consequently, that the rate-determining step of the overall reaction is the release of the first water molecule from the inner coordination sphere of the metal ion. It has been suggested [22] that intramolecular hydrogen bond in the monoanions of dicarboxylic acids is almost negligible when $\Delta pK (= pK_2 - pK_1) \leq 4$, whereas it becomes increasingly important as ΔpK increases. Accordingly, the ΔpK values of DEMA and CPRDA (see Table I) would indicate [18, 23, 24] the existence of significant intramolecular hydrogen bonding in their monoanions. Therefore, bearing in mind that the substitution of the first coordinated water molecule leads to the formation of the protonated intermediate monodentate complex $[\text{Fe}(\text{H}_2\text{O})_4(\text{OH})(\text{HA})]^+$, the lower rates of the reactions involving these monoanions would be related to the relatively slow process of proton loss from these intermediate complexes, where intramolecular hydrogen bonding would exist as well as in the free monoanions. This conclusion would be further supported by the fact that the rates of the reactions between $\text{Ni}(\text{H}_2\text{O})_6^{2+}$ and the same monoanions are also determined [24] by the deprotonation of the intermediate complexes $[\text{Ni}(\text{H}_2\text{O})_5\text{HA}]^+$, whereas with the monoanions of dicarboxylic acids having $\Delta pK < 4$ the rate-determining step is the release of the first coordinated water molecule [24, 25].

The second explanation assumes, on the contrary, that the reactions involving the monoanions of DEMA and CPRDA follow the "normal" dissociative mechanism. The enhanced rates observed with the remaining anions would be then attributable to the occurrence of the "internal conjugate base" (ICB) mechanism proposed by Rorabacher [15] to account for the unusually high rates of the reactions of nickel(II) ion with polyamines. According to this mechanism (applicable to other metal ions), the formation of a hydrogen bond between a basic donor atom of the incoming chelating ligand and a hydrogen

atom of one of the coordinated water molecules stabilizes the outer-sphere complex while favouring the subsequent water release. As a consequence, the more basic the ligand, the more enhanced the reaction rates. Table I shows that just the monoanions of DEMA and CPRDA exhibit significantly lower basicities (pK_1), providing thus support to the possible occurrence of the ICB mechanism with the other more basic monoanions. It should also be noted that the rate constants k_{64} for DEMA and CPRDA are remarkably similar to those seen above for the reactions with simple univalent ligands. The same ICB mechanism was previously proposed by Tanaka and co-workers [5] for the corresponding reaction involving nitrilotriacetate monoanion and was also extended to the monoanions of the malonic acid derivatives studied by us previously [1]. According to these Authors, however, these monoanions were considered to act as hydrogen atom donors and the hydroxo group of FeOH^{2+} as the basic acceptor in the formation of the hydrogen bonding stabilizing the outer-sphere complex. The observed trend of the reactivity of the monoanions of the dicarboxylic acids examined is not in agreement with this view because the monoanions of DEMA and CPRDA are the less dissociable acids (high pK_2), indicating thus the hydrogen bonding formation mentioned above.

With respect to the other kinetically indistinguishable reactions (b) and (f), if it is assumed, analogously to what previously made [1], that $k_{84}K_{\text{OH}}/K_1K_2 \gg k_{52}/K_2$, all the estimated rate constants k_{84} (see Table IV) take quite similar values even though a slight decrease with increasing steric hindrance of the substituent groups is observed. These k_{84} values are within the range of those obtained with the majority of the neutral ligands so far investigated [1, 2, 4, 6-8, 10, 12] [$(1-7) \times 10^3 M^{-1} \text{sec}^{-1}$ at 20-25 °C and $\mu = 0.1-1.0M$ for HF, HN_3 , HCO_2H , $\text{CH}_3\text{CO}_2\text{H}$, $\text{CH}_2\text{ClCO}_2\text{H}$, $\text{C}_2\text{H}_5\text{CO}_2\text{H}$, substituted phenols, thionyltrifluoroacetone, catechol, monoanion of sulfosalicylic acid (this ion acts as neutral ligand [4]) and mandelic, salicylic, iminodiacetic acids; values outside this range have been also found [1, 6, 7, 9, 11-13] for some ligands]. Bearing in mind that k_{84} is a composite rate constant involving the association constant for the outer-sphere complex, the observed k_{84} variation can be reasonably attributed to the effects of the substituent groups upon the association constant [1]. As a consequence, reaction (f) occurs by a dissociative mechanism, the rate-determining step being the release of the first coordinated water molecule.

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