Kinetics of the Reactions of Nickel(II) Ion with Dicarboxylic Acids in Dioxan–Water

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The kinetics of nickel(II) chelation with malonic acid and its methyl and n-butyl derivatives and with cyclopropane-1,1-dicarboxylic acid have been studied at 25 °C and ionic strength 0.10 mol dm^{-3} in dioxan–water (25 : 75 w/w) over a wide acidity range by the temperature-jump method. The kinetic data are discussed and compared with those obtained previously in water.

IN previous studies[1-4] we investigated the kinetics of formation of nickel(II) monochelate complexes with several mono- and di-substituted malonic acids in water. The results showed that, in most cases, chelate-ring closure contributes negligibly to the rate-limiting process and that the basicity and the steric hindrance of the bidentate ligand affect mainly the chelate-ring opening and the rate of the reaction between the nickel(II) ion and the monoprotonated ligand. In particular, the rate of the last reaction was found to be determined by deprotonation of the intermediate unidentate complex [see reaction (5) in this paper] when the reacting ligand is a strongly basic monoanion (*i.e.* monoanions of diethyl- and di-n-butyl-malonic acids and of cyclopropane-1,1-dicarboxylic acid), whereas with other monoanions the rate-determining step is loss of the first co-ordinated water molecule. As to the rate of chelate-ring opening, this decreases significantly with increasing basicity of the dianion co-ordinated to nickel(II), but for dianions of similar basicity an increase in the substituent steric hindrance somewhat facilitates the ring opening.

In the present paper we report the temperature-jump kinetic results at 25 °C and ionic strength 0.10 mol dm^{-3} for the chelation of nickel(II) with malonic (H_2mal), methylmalonic (H_2mmal), n-butylmalonic (H_2bmal), and cyclopropane-1,1-dicarboxylic acids (H_2cpda) in dioxan–water (25 : 75 w/w). The dianions mal, mmal, and bmal have similar basicity[5] ($\mathrm{p}K_2^{\mathrm{H}} = 6.00$—6.22), whereas cpda[5] is much more basic ($\mathrm{p}K_2^{\mathrm{H}} = 8.16$).

Kinetic and equilibrium studies on various organic solvent–water mixtures have revealed that changes in the properties of the solvent medium (dielectric constant, structure, basicity, *etc.*) greatly affect the rates and the thermodynamic quantities of reactions involving ionic species. The effects of the addition of dioxan to water on the dissociation constants of several substituted malonic acids were studied previously by us[5] and it was found that the basicity of both the mono- and di-anions increases markedly on passing from water to dioxan–water (25 : 75 w/w). In the present investigation we examine the effects of changes in the solvent properties upon the rate of the various steps involved in the nickel(II) monochelate complex formation. The stability constants of these complexes have also been estimated using a kinetic method, as described below. We have chosen the dioxan–water (25 : 75 w/w) mixture mainly in order to compare our value for the stability constant of the nickel malonate complex with that estimated spectrophotometrically by Underdown *et al.*[6] and thus to support the validity of the kinetic method used for the evaluation of all the stability constants.

EXPERIMENTAL

The dicarboxylic acids and dioxan were prepared and purified as described elsewhere.[2,4,5] Fluka reagent-grade nickel(II) perchlorate, very pure Fluka sodium perchlorate and 70% perchloric acid were used to prepare stock solutions of these substances in dioxan–water (25 : 75 w/w), allowance being made, when necessary, for water content. Nickel(II) perchlorate solution was standardized by titration with ethylenediaminetetra-acetate. Solutions of dicarboxylic acids and indicators (Chlorophenol Red, Bromocresol Green, and Bromochlorophenol Blue) in dioxan–water (25 : 75) were prepared by weight before use. The indicators were necessary to follow the course of the relaxation process.

The pH of the solutions used for the kinetic experiments was measured by a Radiometer pH meter 26 equipped with a Radiometer type GK 2301C combined electrode having a saturated salt (NaCl) solution in dioxan–water (25 : 75). The pH meter readings were converted into hydrogen-ion concentrations by means of a calibration curve made as described before.[5]

The kinetic measurements were performed at 25 °C and $I = 0.10$ mol dm^{-3} (supporting electrolyte $\mathrm{Na[ClO_4]}$) with the temperature-jump apparatus and experimental procedure adopted previously.[1-4]

RESULTS AND DISCUSSION

According to the spectrophotometric investigation of Underdown *et al.*[6] on the stability of nickel malonate in dioxan–water mixtures containing small amounts of dioxan (maximum dioxan content = 25% w/w corresponding to a mol fraction of dioxan of 0.064), the predominant equilibria existing in these solvent mixtures are the same as those in water. Moreover, the kinetic data from the present work are consistent with the reaction mechanism proposed previously[1-4] for the formation of the nickel(II) monochelate complexes with substituted malonic acids in water. According to this mechanism, two reactions contribute to the formation of the nickel(II) monochelate complex under the experimental conditions used, *i.e.* the reactions of nickel ion with the monoanionic [$\mathrm{H}\overset{\frown}{\mathrm{O\,O}}{}^{-}$; reactions (2), (4)—(6)] and dianionic [$\overset{\frown}{\mathrm{O\,O}}{}^{2-}$; reactions (1), (3), (6)] forms of the bidentate ligand. The derived equation for the relax-

TABLE 1

Kinetic data[a] at constant acidity and equilibrium constants in dioxan–water (25 : 75 w/w) ($[\mathrm{H}^+] = 1.00 \times 10^{-5}$ mol dm^{-3}, 25 °C, $I = 0.10$ mol dm^{-3})

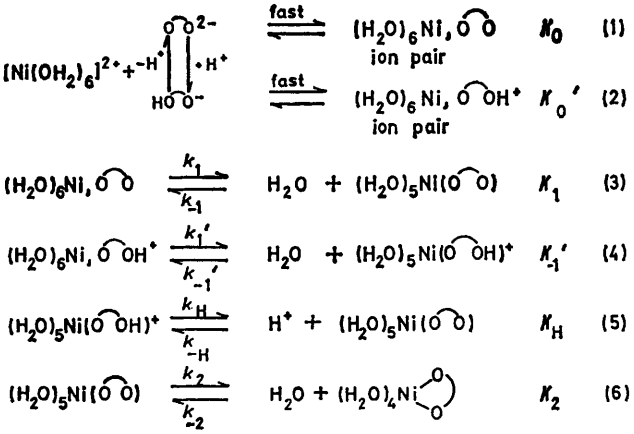
$\dfrac{10^4[\mathrm{Ni}]_T}{\text{mol dm}^{-3}}$ [b]	$\dfrac{10^4[\mathrm{H\overset{\frown}{O\,O}H}]_T}{\text{mol dm}^{-3}}$ [c]	$\dfrac{10^4\left(\dfrac{[\mathrm{Ni}^{2+}]}{1+\alpha+\beta} + [\overset{\frown}{\mathrm{O\,O}}{}^{2-}]\right)}{\text{mol dm}^{-3}}$	$\dfrac{10^3\tau}{\text{s}}$
Malonic acid[d]			
7.00	5.00	5.22	5.5
7.00	16.0	6.64	6.3
8.00	8.00	6.53	5.5
10.0	10.0	8.28	5.0
12.0	10.0	9.74	5.0
13.0	12.0	10.7	4.3
15.0	15.0	12.5	4.2
18.0	17.0	14.9	3.7
20.0	10.0	15.6	3.6
20.0	15.0	16.2	3.2
25.0	20.0	20.3	3.0
35.0	25.0	27.9	2.4
45.0	30.0	35.2	2.2
55.0	30.0	42.6	1.9
Methylmalonic acid[e]			
7.00	5.00	4.72	2.5
7.00	16.0	6.02	2.6
10.0	10.0	7.47	2.5
12.0	10.0	8.80	2.2
13.0	12.0	9.70	2.1
15.0	15.0	11.3	1.8
20.0	5.00	12.6	1.7
20.0	10.0	14.1	1.6
20.0	15.0	14.7	1.5
30.0	15.0	21.4	1.3
35.0	25.0	25.3	1.2
40.0	20.0	28.5	1.1
45.0	30.0	32.1	0.96
55.0	30.0	38.8	0.87
65.0	50.0	44.5	0.87
70.0	60.0	47.1	0.81
85.0	60.0	56.6	0.67
n-Butylmalonic acid[f]			
6.00	5.00	3.46	2.0
7.00	5.00	3.99	2.2
8.00	8.00	5.08	2.0
10.0	10.0	6.51	1.9
11.0	9.00	6.96	1.9
12.0	10.0	7.70	1.8
15.0	10.0	9.47	1.6
15.0	15.0	10.0	1.7
20.0	15.0	13.1	1.5
20.0	20.0	13.5	1.5
25.0	15.0	16.2	1.3
30.0	20.0	19.7	1.1
35.0	25.0	23.1	0.98
40.0	30.0	26.4	0.93
45.0	35.0	29.6	0.93
50.0	40.0	32.7	0.82
55.0	45.0	35.7	0.81
60.0	50.0	38.7	0.77
Cyclopropane-1,1-dicarboxylic acid[g]			
5.00	5.00	1.20	27
7.00	7.00	2.26	25
10.0	7.00	3.21	22
13.0	8.00	4.68	20
17.0	12.0	8.75	15
20.0	20.0	15.8	14
23.0	20.0	18.1	12
27.0	25.0	25.4	9.9
30.0	30.0	32.3	10
35.0	30.0	37.7	8.3
40.0	30.0	42.9	8.2

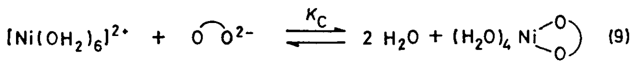
[a] Bromocresol Green as indicator. [b] Total molar concentration of nickel perchlorate. [c] Total molar concentration of ligand. [d] $K_C = (7.8 \pm 0.9) \times 10^2$ dm^3 mol^{-1}; $K_1^H = 9.5 \times 10^{-4}$ and $K_2^H = 10.0 \times 10^{-7}$ mol dm^{-3} (ref. 5). [e] $K_C = (6.9 \pm 0.6) \times 10^2$ dm^3 mol^{-1}; $K_1^H = 4.0 \times 10^{-4}$ and $K_2^H = 9.1 \times 10^{-7}$ mol dm^{-3} (ref. 5). [f] $K_C = (6.7 \pm 0.4) \times 10^2$ dm^3 mol^{-1}; $K_1^H = 4.07 \times 10^{-4}$ and $K_2^H = 6.0 \times 10^{-7}$ mol dm^{-3} (ref. 5). [g] $K_C = (5.1 \pm 0.7) \times 10^3$ dm^3 mol^{-1}; $K_1^H = 1.17 \times 10^{-2}$ and $K_2^H = 6.9 \times 10^{-9}$ mol dm^{-3} (ref. 5).

ation time τ associated with the complexation reactions is [2-4] (7) (square brackets indicate equilibrium concentrations) where A is given by equation (8), a, b, and c are constant quantities related to the rate constants, K_C is the equilibrium constant for reaction (9), and α and β are quantities dependent on the equilibrium concentrations of the predominant chemical species present in solution. These concentrations can be calculated from the concentrations of hydrogen ion, nickel perchlorate, and ligand added if K_C and the dissociation constants of the ligand are known.

$$\frac{1}{\tau A} = \frac{a + b[\mathrm{H}^+]}{1 + c[\mathrm{H}^+]} \qquad (7)$$

$$A = \frac{[\mathrm{Ni}^{2+}]}{1 + \alpha + \beta} + [\overset{\frown}{\mathrm{O\,O}}{}^{2-}] + \frac{1}{K_C} \qquad (8)$$





The first (K_1^H) and second (K_2^H) dissociation constants of the dicarboxylic acids examined have been estimated previously [5] and are reported in Table 1. The equilibrium constants K_C in dioxan–water (25 : 75 w/w) have been evaluated in the present work from kinetic measurements at constant hydrogen-ion concentration ($[\mathrm{H}^+] =$

1.00×10^{-5} mol dm^{-3}) and at various concentrations of nickel perchlorate and ligand (Table 1). From equations (7) and (8) it can be shown that at constant acidity the equilibrium constant K_C is equal to the ratio of the slope to the intercept obtained by plotting $1/\tau$ against $\{[\mathrm{Ni}^{2+}]/(1 + \alpha + \beta)\} + [\widehat{\mathrm{O\,O}}^{2-}]$. Since the equilibrium concentrations were unknown, an iterative program run on an IBM 370/145 computer was used to estimate the equilibrium constant, as carried out previously[7] for the corresponding complexes of iron(III). The estimated K_C values and their standard deviations are given in Table 1 together with the final values of $\{[\mathrm{Ni}^{2+}]/(1 + \alpha + \beta)\} + [\widehat{\mathrm{O\,O}}^{2-}]$.

Similar measurements were also carried out with some other dicarboxylic acids, such as di-n-butylmalonic acid, but they were discontinued because of the small relaxation effect observed. The equilibrium constant for the formation of nickel monomalonate complex in the same dioxan–water mixture considered in the present work was found previously by Underdown *et al.*[6] to be equal to 2.62×10^4 dm^3 mol^{-1} at 25 °C and zero ionic strength. If the Davies equation is used to estimate the activity coefficients of bivalent ions[5] ($\gamma_2 = 0.182$, using the value of 56.29 for the dielectric constant of the mixed solvent[5]) the calculated K_C value at $I = 0.10$ mol dm^{-3} is 8.7×10^2 dm^3 mol^{-1}, in fair agreement with that estimated in the present work. The stabilities of the nickel complexes examined in dioxan–water follow the same order observed in water[1-3] (*i.e.* cpda > mal > mmal > bmal) as do the basicities[5] of the dianionic ligands (*i.e.* cpda > bmal > mmal > mal), indicating that the effects of the substituent groups in malonic acid are analogous in the two media.

Kinetic measurements at various acidities (Table 2)

TABLE 2

Experimental conditions[a] and relaxation times for the reaction of nickel(II) ion with dicarboxylic acids in dioxan–water (25 : 75 w/w) (25 °C, $I = 0.10$ mol dm^{-3})

$\dfrac{10^4[\mathrm{Ni}]_\mathrm{T}{}^{b}}{\mathrm{mol\ dm^{-3}}}$	$\dfrac{10^4[\mathrm{H\widehat{O\,O}H}]_\mathrm{T}{}^{c}}{\mathrm{mol\ dm^{-3}}}$	$\dfrac{10^6[\mathrm{H^+}]}{\mathrm{mol\ dm^{-3}}}$	$\dfrac{10^3\tau_\mathrm{obs.}}{\mathrm{s}}$	$\dfrac{10^3\tau_\mathrm{calc.}}{\mathrm{s}}$
Malonic acid				
20.0	10.0	1.19	3.5	3.7
30.0	20.0	2.19	2.8	2.8
30.0	20.0	4.70	2.4	2.5
20.0	10.0	5.51	2.7	3.1
35.0	20.0	6.24	2.2	2.2
40.0	30.0	7.66	2.3	1.9
20.0	10.0	15.5	2.8	2.9
25.0	20.0	16.2	2.7	2.4
25.0	20.0	20.8	2.1	2.4
30.0	20.0	23.9	2.3	2.3
30.0	20.0	32.1	2.2	2.4
20.0	10.0	38.5	3.4	3.1
30.0	20.0	50.6	2.8	2.7
25.0	15.0	58.0	2.7	3.0
30.0	20.0	68.8	2.9	2.8
35.0	20.0	76.2	2.7	2.8
25.0	15.0	104	3.3	3.1
35.0	25.0	112	2.8	2.9
30.0	20.0	114	3.1	3.0
35.0	25.0	138	2.9	3.0
35.0	20.0	151	3.1	3.0
n-Butylmalonic acid				
30.0	20.0	1.52	1.2	1.3
45.0	35.0	2.12	1.0	0.98
50.0	40.0	2.60	1.0	0.89
35.0	20.0	3.96	0.95	1.0
30.0	20.0	4.59	0.95	1.1
45.0	35.0	5.70	0.88	0.81
40.0	30.0	8.02	0.86	0.85
45.0	30.0	8.30	0.86	0.79
45.0	35.0	11.0	0.78	0.79
30.0	20.0	13.2	0.92	1.0
40.0	30.0	15.5	0.87	0.88
55.0	40.0	17.8	0.85	0.76
35.0	25.0	20.4	0.97	1.0
40.0	30.0	23.6	0.90	0.97
60.0	50.0	29.3	0.86	0.85
40.0	30.0	34.4	1.1	1.1
30.0	20.0	37.2	1.3	1.2
15.0	10.0	43.2	1.5	1.4
50.0	40.0	45.7	1.0	1.0
35.0	20.0	49.5	1.1	1.2
35.0	25.0	55.4	1.2	1.2
25.0	15.0	58.0	1.4	1.3
55.0	45.0	60.7	1.1	1.1
35.0	25.0	65.0	1.2	1.2
Methylmalonic acid				
40.0	30.0	2.24	1.5	1.4
50.0	40.0	2.72	1.3	1.2
30.0	20.0	3.78	1.5	1.5
40.0	30.0	6.10	1.2	1.2
25.0	10.0	7.66	1.6	1.6
35.0	25.0	15.5	1.2	1.3
50.0	40.0	19.9	1.1	1.1
30.0	20.0	23.1	1.5	1.5
25.0	10.0	38.5	1.8	1.7
60.0	50.0	42.2	1.2	1.2
35.0	25.0	47.3	1.5	1.5
30.0	20.0	54.2	1.6	1.6
40.0	30.0	60.7	1.5	1.5
30.0	20.0	76.2	1.7	1.6
40.0	30.0	81.6	1.6	1.5
45.0	35.0	83.5	1.3	1.5
45.0	35.0	87.4	1.4	1.5
50.0	40.0	93.6	1.4	1.4
45.0	35.0	100	1.5	1.5
40.0	30.0	127	1.5	1.5
Cyclopropane-1,1-dicarboxylic acid				
25.0	20.0	2.46	4.3	4.5
25.0	20.0	4.15	5.8	6.0
25.0	25.0	5.20	6.1	5.9
35.0	30.0	7.16	6.2	5.8
20.0	15.0	11.3	16	15
20.0	20.0	17.8	19	17
50.0	40.0	19.5	10	10
45.0	35.0	22.1	11	12
50.0	40.0	24.4	11	12
25.0	20.0	28.7	19	18
45.0	40.0	34.4	14	15
40.0	30.0	39.4	17	16
60.0	50.0	54.2	14	15
40.0	40.0	68.0	17	17
45.0	40.0	93.6	18	17
50.0	45.0	105	16	16
55.0	50.0	123	16	16
60.0	50.0	129	15	16
60.0	55.0	151	16	16
50.0	34.0	173	16	16

[a] Chlorophenol Red, Bromocresol Green, and Bromochlorophenol Blue used as indicators. [b,c] As in Table 1.

TABLE 3

Kinetic data for the formation and dissociation of nickel(II) monochelate complexes with dicarboxylic acids in dioxan–water (25 : 75 w/w) (25 °C, I = 0.10 mol dm^{-3})

	H_2mal	H_2mmal	H_2bmal	H_2cpda
$10^{-5}a$/dm^3 mol^{-1} s^{-1}	0.80	1.3	1.6	1.9
$10^{-9}b$/dm^6 mol^{-2} s^{-1}	7.5	10.5	25	7.5
$10^{-4}c$/dm^3 mol^{-1}	2.8	2.0	4.3	2.2
$k_2/(k_{-1} + k_2)$	0.70	0.75	0.73	0.44
k_2/k_{-1}	2	3	3	0.8
$10^{-5}k_1K_0$/dm^3 mol^{-1} s^{-1}	1.1	1.7	2.2	4.3
$10^{-2}k_{-2}$/s^{-1}	3.4	7.6	8.7	0.67
$10^{-2}k_{-1}K_2^{-1}$/s^{-1}	1.5	2.5	3.3	0.84
$10^{-7}k_{-1}'k_{-\mathrm{H}}[K_2(k_{-1}' + k_\mathrm{H})]^{-1}$/dm^3 mol^{-1} s^{-1}	1.4	2.0	5.1	0.33
$10^{-3}k_1'k_\mathrm{H}K_0'(k_{-1}' + k_\mathrm{H})^{-1}$/dm^3 mol^{-1} s^{-1}	11	13	21	0.12

TABLE 4

Some kinetic data for the formation and dissociation of nickel(II) monochelate complexes with dicarboxylic acids in water and in dioxan–water (25 : 75 w/w) (25 °C, I = 0.10 mol dm^{-3})

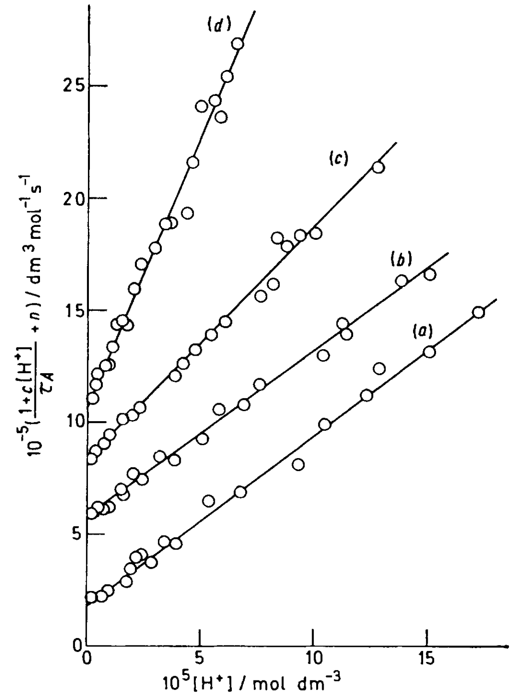
Ligand	k_2/k_{-1}	$10^{-4}k_1K_0$/dm^3 mol^{-1} s^{-1}	$10^{-3}k_1'k_\mathrm{H}K_0'(k_{-1}' + k_\mathrm{H})^{-1}$/dm^3 mol^{-1} s^{-1}		$10^{-2}k_{-2}$/s^{-1}	pK_1^H	pK_2^H	ΔpK^H= pK_2^H − pK_1^H
			$10^{-3}k_1'K_0'$ [a]	$10^{-3}k_\mathrm{H}K_1'K_0'$ [b]				
(*a*) In water								
H_2mal [c]		7.0	3.1			2.70	5.26	2.56
H_2mmal [d]	13	7.3	5.1		22	2.94	5.40	2.46
H_2bmal [d]	16	7.5	4.0		39	2.81	5.50	2.69
H_2cpda [e]	18	8.6		0.12	2.0	1.68	7.22	5.54
(*b*) In dioxan–water								
H_2mal	2	11	11		3.4	3.02	6.00	2.98
H_2mmal	3	17	13		7.6	3.40	6.04	2.64
N_2bmal	3	22	21		8.7	3.39	6.22	2.83
H_2cpda	0.8	43		0.12	0.67	1.93	8.16	6.23

[a] With $k_\mathrm{H} \gg k_{-1}'$ (see text). [b] With $k_\mathrm{H} \ll k_{-1}'$ (see text). [c] Ref. 1. [d] Ref. 2. [e] Ref. 3.

allow us to estimate for each ligand the quantities a, b, and c of equation (7) using a non-linear least-squares program.[3] The values of these quantities are collected in Table 3 together with those of the rate constants obtained by appropriate combination of them.[2-4] The Figure shows linear plots of $(1 + c[\mathrm{H}^+])/\tau A$ against $[\mathrm{H}^+]$ in accordance with equation (7), and good agreement is obtained (*cf.* Table 2) between the observed relaxation times and those calculated by using the given a, b, and c values and equation (7).

Some kinetic data from the present work are compared in Table 4 with those obtained previously in water. It can be seen that for all the ligands examined the k_2/k_{-1} values are smaller in the presence of dioxan, indicating that the contribution of chelate-ring closure to the limiting rate in the overall chelate-formation process becomes significant in the dioxan–water mixture. Moreover, since the rate constant k_{-1} is expected[2,8] to decrease in the solvent mixture because of the enhanced basicity of the co-ordinated carboxylate group (*cf.* Table 4), the lower k_2/k_{-1} values suggest that the rate constant k_2 is diminished by a factor higher than 6. The decreased ring-closure rate in dioxan–water, which cannot be attributed to the reduced dielectric constant of the medium, may be related to the effects of the bulkier dioxan molecules upon the rotation of the free carboxylate group and/or upon the water structure, slowing down both the release of the co-ordinated water molecule and the formation of the second metal–oxygen bond.

The constants k_1K_0 for the formation of the unidentate complexes $(H_2O)_5Ni(\overset{\frown}{O\,O})$ are larger in dioxan–water than in water, in accordance with the enhancement of the ion-pair formation constant, K_0, in the medium at lower dielectric constant.[9] The observed dependence of the



Plots of $(1 + c[\mathrm{H}^+])/\tau A$ against $[\mathrm{H}^+]$ for cyclopropane-1,1-dicarboxylic acid (*a*, n = 0), malonic acid (*b*, n = 5), methylmalonic acid (*c*, n = 7), and n-butylmalonic acid (*d*, n = 9)

k_1K_0 values on the nature of the ligand is difficult to explain, being attributable either to the variation of k_1 or K_0, or to a change in the values of both k_1 and K_0.

As to the reactions of nickel(II) ion with the monoanionic ligands $\mathrm{H}\widehat{\mathrm{OO}}^{-}$, the values of the quantity $k_1'k_{\mathrm{H}}K_0'/(k_{-1}' + k_{\mathrm{H}})$ in dioxan–water show a trend similar to that observed in water, that is the $k_1'k_{\mathrm{H}}K_0'/(k_{-1}' + k_{\mathrm{H}})$ value for Hcpda is markedly smaller than those found for the other ligands. Therefore, since the conclusions drawn previously for the reactions in water [2-4] also apply to the dioxan–water mixture, the limiting case $k_{\mathrm{H}} \gg k_{-1}'$ occurs for malonic acid and its methyl and n-butyl derivatives, and, consequently, the quantity $k_1'k_{\mathrm{H}}K_0'/(k_{-1}' + k_{\mathrm{H}})$ reduces to $k_1'K_0'$ (*cf.* Table 4), the slower step being reaction (4). The higher $k_1'K_0'$ values found in the presence of dioxan can be ascribed to the larger K_0' values in the solvent mixture with decreased dielectric constant.[9] As to the reaction involving the Hcpda monoanion, the opposite limiting case occurs [$k_{\mathrm{H}} \ll k_{-1}'$ and $k_1'k_{\mathrm{H}}K_0'/(k_{-1}' + k_{\mathrm{H}}) = k_{\mathrm{H}}K_1'K_0'$] and the deprotonation of the intermediate $(\mathrm{H_2O})_5\mathrm{Ni}(\widehat{\mathrm{OO}}\mathrm{H})^{+}$ [reaction (5)] now becomes the slower reaction. The lower rate of the proton-transfer process (5) observed for Hcpda (and for other monoanions of dicarboxylic acids with $\Delta\mathrm{p}K^{\mathrm{H}} = \mathrm{p}K_2^{\mathrm{H}} - \mathrm{p}K_1^{\mathrm{H}} > 4$) was previously ascribed to the existence of intramolecular hydrogen bonding both in the free monoanion [10] and in the monoanion co-ordinated to nickel.[3,4] By using the mean $k_1'K_0'$ value of 15×10^3 dm^3 mol^{-1} s^{-1} obtained for the remaining ligands examined in dioxan–water, it can be calculated from the expression $k_1'k_{\mathrm{H}}K_0'/(k_{-1}' + k_{\mathrm{H}}) = 0.12 \times 10^3$ dm^3 mol^{-1} s^{-1} that $k_{-1}'/k_{\mathrm{H}} = 124$. The corresponding value estimated in water is 39.[3] Therefore, if we also consider that the higher basicity of the monoanions in the solvent mixture (*cf.* Table 4) is expected [2,8] to cause a decrease in the rate constant k_{-1}', we can conclude that the rate of the deprotonation process (5) is decreased to a significant extent in dioxan–water. This is in agreement with the larger $\Delta\mathrm{p}K^{\mathrm{H}}$ value found in the presence of dioxan (Table 4), indicating a stronger intramolecular hydrogen bonding in the Hcpda monoanion.[5]

The observed dependence of the rate of chelate-ring opening (k_{-2}) on the nature of the ligand in dioxan–water (Table 4) is analogous to that found in water.[2-4] In fact, the steric hindrance of the substituent group in malonic acid accelerates to some extent the ring opening when the co-ordinated dianions exhibit similar basicity, whereas the rate decreases significantly in the case of the very basic cpda dianion. Comparison of the k_{-2} values obtained in the two different media shows that the ring opening is slower in dioxan–water, in agreement with the enhanced basicity of the co-ordinated dianions in the solvent mixture.

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