Kinetics of the Reactions of the Nickel(II) Ion with Methyl- and n-Butylmalonic Acids

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The kinetics of the reactions of nickel(II) with methyl- and n-butyl-malonic acids have been studied in aqueous solution by the temperature-jump method, at ionic strength 0·10M and 25 °C, over the acidity range from 2×10^{-6} to 5×10^{-4}M. The kinetic data indicate that two competitive reaction paths lead to 1 : 1 chelate formation, *i.e.* the nickel ion reacts with dianionic and monoanionic forms of the ligands. The results obtained permit us to establish that the rate constant for ring closure is larger than that for dissociation of the monodentate complex $(H_2O)_5Ni(O_2C{\cdot}CHR{\cdot}CO_2)$ (R = Me or Bu^n; $O_2C{\cdot}CHR{\cdot}CO_2{}^{2-}$ = dianionic form of the ligand).

At low acidities, the loss of the first water molecule co-ordinated to nickel(II) appears to be the rate-determining step in the overall chelate-formation process. Values are assigned to rate and equilibrium constants for each of the steps involved in this process.

The formation of metal monochelate complexes with bidentate ligands in aqueous solution implies the replacement of two co-ordinated water molecules. For most chelate-formation reactions involving bivalent transition-metal ions, the overall rate appears [1-4] to be determined by the release of the first water molecule from the inner co-ordination sphere of the metal ion (' normal substitution '). Support for this is generally found in the similarity of observed rate constants for reactions of a given metal ion with mono- and bi-dentate ligands of the same charge.[1-4] In some cases, however, the overall rate of chelate formation is slower than expected for a ' normal ' substitution and it has been suggested [4-6] that the rate-determining step is the ring-closure process (' sterically controlled substitution ').

In the particular case of monochelate complexes of nickel(II) with anionic ligands such as oxalate, malonate, *meso*-tartrate, and β-alanate, Hoffmann [6] was able to estimate, making certain assumptions, the rate constants for the various steps involved in chelate formation. According to these estimates, the rate constants for ring closure are smaller than those for formation of the intermediate monodentate complex and they are, moreover, comparable to (in the case of the oxalate and malonate anions) or smaller than (for the other ligands considered) the rate constants for dissociation of the monodentate complex.

The present study is part of a programme of research undertaken in order to provide more information on the kinetics and mechanism of metal chelate formation and, in particular, to examine the effects of structural changes in the bidentate ligands on the rate of chelate ring closure. It deals with the kinetics of the reactions of nickel(II) with methyl- and n-butyl-malonic acids which form six-membered chelate rings, and can be considered to be a continuation of the previous kinetic study on nickel(II) monomalonate complex formation.[2] The investigation has been carried out in aqueous solution, at 25 °C and ionic strength 0·10M, over a wide acidity range ($2 \times 10^{-6}\text{M} \leqslant [H^+] \leqslant 5 \times 10^{-4}\text{M}$) using the temperature-jump relaxation method.

EXPERIMENTAL

Commercial methylmalonic acid (Fluka) and n-butylmalonic acid, obtained [7] by basic hydrolysis of the diethyl ester (Fluka), were purified before use as described previously.[8] Fluka reagent grade $Ni(ClO_4)_2,6H_2O$ was used to prepare an aqueous stock nickel(II) ion solution which was standardized by titration with edta.[9] Stock solutions of the dicarboxylic acids, sodium perchlorate (very pure Fluka product), and indicators (Chlorophenol Red, Bromocresol Green, and Bromochlorophenol Blue) were prepared by weight.

Solutions for kinetic experiments were prepared by mixing aliquot portions of stock solutions of nickel(II) perchlorate, dicarboxylic acid, and the appropriate indicator. The latter was used to follow the course of the relaxation process. The ionic strength of the solutions was adjusted to 0·10M with stock sodium perchlorate solution and the pH by addition of standard NaOH and/or $HClO_4$. The pH measurements were made with a Radiometer 26 pH meter equipped with glass and calomel electrodes. Hydrogen-ion concentrations were calculated from pH values using the expression $-\log [H^+] = \text{pH} - 0{\cdot}11$, where $-0{\cdot}11$ (= $\log \gamma\pm$) was evaluated (at 25 °C and I = 0·10M) from the Davies equation.[10]

The temperature-jump experiments were carried out at wavelengths of 580 (in the presence of Chlorophenol Red), 610 (in the presence of Bromocresol Green), and 590 nm (in the presence of Bromochlorophenol Blue) with the apparatus described elsewhere; [11] a tungsten lamp was used in the present work. The magnitude of the temperature-jump was 3·7 °C for a 30 kV discharge. For each experiment a single relaxation process was observed. Blank experiments on solutions containing only the ligand and the indicator, or with the metal ion and the indicator in the same experi-

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[9] A. I. Vogel, ' A Text-book of Quantitative Inorganic Analysis,' 3rd edn., Longmans, Green, and Co., London, 1961, p. 435.

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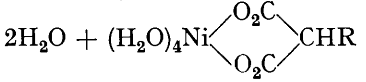
mental conditions, did not show any discernible relaxation effect. The relaxation times, τ, for the various solutions were determined from at least five photographs of the oscilloscope traces and are affected by a maximum error of *ca.* ±10%. All calculations were made with the help of computer programs run on an Olivetti Programma 101.

RESULTS AND DISCUSSION

According to potentiometric investigations,[12,13] the only important equilibria which exist in aqueous acid solutions containing nickel(II) ions and the dicarboxylic acids examined are (1)—(3) (R = Me or Bu^n; $O_2C{\cdot}CHR{\cdot}CO_2^{2-}$ = dianionic form of the ligand). In addition to these, for the solutions under study, equilibrium (4) (HIn = indicator) must also be considered.

$$\mathrm{Ni(H_2O)_6^{2+} + O_2C{\cdot}CHR{\cdot}CO_2^{2-}} \overset{K_O}{\rightleftharpoons}$$



(1)

$$\mathrm{HO_2C{\cdot}CHR{\cdot}CO_2H} \overset{K_1^H}{\rightleftharpoons} \mathrm{HO_2C{\cdot}CHR{\cdot}CO_2^- + H^+} \quad (2)$$

$$\mathrm{HO_2C{\cdot}CHR{\cdot}CO_2^-} \overset{K_2^H}{\rightleftharpoons} \mathrm{O_2C{\cdot}CHR{\cdot}CO_2^{2-} + H^+} \quad (3)$$

$$\mathrm{HIn} \overset{K_i}{\rightleftharpoons} \mathrm{In^- + H^+} \quad (4)$$

The various pertinent equilibrium constants, enabling evaluation of the equilibrium concentrations of the species involved in reactions (1)—(4), are listed in Table 1. A summary of the experimental conditions, together with the observed relaxation times, is given in Table 2.

The kinetic data obtained for both dicarboxylic acids examined are consistent with the following reaction mechanism:

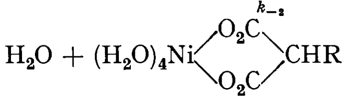
$$\mathrm{Ni(H_2O)_6^{2+}} + \begin{array}{l} \mathrm{O_2C{\cdot}CHR{\cdot}CO_2^{2-}} \underset{\text{v. fast}}{\overset{K_0}{\rightleftharpoons}} \mathrm{(H_2O)_6Ni,O_2C{\cdot}CHR{\cdot}CO_2} \quad (5) \\ \quad -\mathrm{H^+} \Big\uparrow\!\!\Big\downarrow +\mathrm{H^+} \\ \mathrm{HO_2C{\cdot}CHR{\cdot}CO_2^-} \underset{\text{v. fast}}{\overset{K_0'}{\rightleftharpoons}} \mathrm{(H_2O)_6Ni,O_2C{\cdot}CHR{\cdot}CO_2H^+} \quad (6) \end{array}$$

$$\mathrm{(H_2O)_6Ni,O_2C{\cdot}CHR{\cdot}CO_2} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{H_2O + (H_2O)_5Ni(O_2C{\cdot}CHR{\cdot}CO_2)} \quad K_1 = k_1/k_{-1} \quad (7)$$

$$\mathrm{(H_2O)_6Ni,O_2C{\cdot}CHR{\cdot}CO_2H^+} \underset{k_{-1}'}{\overset{k_1'}{\rightleftharpoons}} \mathrm{H_2O + (H_2O)_5Ni(O_2C{\cdot}CHR{\cdot}CO_2H)^+} \quad K_1' = k_1'/k_{-1}' \quad (8)$$

$$\mathrm{(H_2O)_5Ni(O_2C{\cdot}CHR{\cdot}CO_2H)^+} \underset{k_{-H}}{\overset{k_H}{\rightleftharpoons}} \mathrm{H^+ + (H_2O)_5Ni(O_2C{\cdot}CHR{\cdot}CO_2)} \quad K_H = k_H/k_{-H} \quad (9)$$

$$\mathrm{(H_2O)_5Ni(O_2C{\cdot}CHR{\cdot}CO_2)} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}}$$



$K_2 = k_2/k_{-2}$ (10)

Here $\mathrm{(H_2O)_6Ni,O_2C{\cdot}CHR{\cdot}CO_2}$ and $\mathrm{(H_2O)_6Ni,O_2C{\cdot}CHR{\cdot}CO_2H^+}$ (R = Me or Bu^n) represent outer-sphere complexes and reaction (9) is to be considered a proton-transfer process involving, probably, the solvent as proton acceptor.

TABLE 1

Equilibrium constants at 25 °C and I = 0·10M

	$10^3K_1^H$ mol l^{-1}	$10^6K_2^H$ mol l^{-1}	K_O l mol^{-1}	10^5K_i mol l^{-1}
Methylmalonic acid [a]	1·15	3·98	417	
n-Butylmalonic acid [b]	1·55	3·15	311	
Chlorophenol Red [c]				0·11
Bromocresol Green [d]				2·0
Bromochlorophenol Blue [d]				10

[a] Ref. 12. [b] Ref. 13. [c] K. Kustin and K. O. Watkins, *Inorg. Chem.*, 1964, **3**, 1706. [d] Refs. 2 and 3.

According to this mechanism two reactions contribute significantly to formation of the nickel monochelate complex over the acidity range investigated: the reactions of the nickel(II) ion with the dianionic ligand $O_2C{\cdot}CHR{\cdot}CO_2^{2-}$ and the corresponding conjugate acid $HO_2C{\cdot}CHR{\cdot}CO_2^-$. An analogous reaction mechanism has been previously proposed for the formation of nickel(II) and cobalt(II) monomalonate complexes [2,3] and, more recently, for the formation [14] of the tris(ethylenediamine)-nickel(II) complex.

Since the protolytic reactions (2)—(4) can be considered to be much more rapid than the complexation reactions, assuming steady-state conditions for the intermediate species, the relaxation time may be related to the rate constants by expression (11), where A, α, β, N, k_f, and k_f' are given by equations (12)—(17) and square

$$1/\tau = k_fA + k_f'[\mathrm{H^+}](A + N)/K_2^H \quad (11)$$

$$A = [\mathrm{Ni^{2+}}]/(1 + \alpha + \beta) + [\mathrm{O_2C{\cdot}CHR{\cdot}CO_2^{2-}}] + 1/K_O \quad (12)$$

$$\alpha = \frac{K_1^H\{1 + [\mathrm{In^-}]/(K_i + [\mathrm{H^+}]) + 2[\mathrm{HO_2C{\cdot}CHR{\cdot}CO_2^-}]/K_1^H\}[\mathrm{H^+}]}{K_1^HK_2^H\{1 + [\mathrm{In^-}]/(K_i + [\mathrm{H^+}]) + 2[\mathrm{HO_2C{\cdot}CHR{\cdot}CO_2^-}]/K_1^H\} + (K_1^H + 2[\mathrm{H^+}])[\mathrm{O_2C{\cdot}CHR{\cdot}CO_2^{2-}}]} \quad (13)$$

$$\beta = \frac{\{1 + [\mathrm{In^-}]/(K_i + [\mathrm{H^+}]) - [\mathrm{O_2C{\cdot}CHR{\cdot}CO_2^{2-}}]/K_2^H\}[\mathrm{H^+}]^2}{K_1^HK_2^H\{1 + [\mathrm{In^-}]/(K_i + [\mathrm{H^+}]) - [\mathrm{O_2C{\cdot}CHR{\cdot}CO_2^{2-}}]/K_2^H\} + 2(K_1^H + 2[\mathrm{H^+}])[\mathrm{O_2C{\cdot}CHR{\cdot}CO_2^{2-}}]} \quad (14)$$

$$N = \frac{[\mathrm{Ni^{2+}}]}{(1 + \alpha + \beta)} \times \left(\frac{\alpha K_2^H\{1 + [\mathrm{In^-}]/(K_i + [\mathrm{H^+}])\} + (\alpha + 2\beta)[\mathrm{O_2C{\cdot}CHR{\cdot}CO_2^{2-}}]}{\{1 + [\mathrm{In^-}]/(K_i + [\mathrm{H^+}])\}[\mathrm{H^+}]} - 1\right) \quad (15)$$

$$k_f = \frac{k_1k_2K_0}{(k_{-1} + k_2) + k_{-1}'k_{-H}[\mathrm{H^+}]/(k_{-1}' + k_H)} \quad (16)$$

$$k_f' = \frac{k_1'k_Hk_2K_0'}{(k_{-1}' + k_H)\{(k_{-1} + k_2) + k_{-1}'k_{-H}[\mathrm{H^+}]/(k_{-1}' + k_H)\}} \quad (17)$$

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TABLE 2

Kinetic data for the reaction of nickel(II) with methyl- and n-butyl-malonic acids (I = 0·10M; t = 25 °C)

$10^4[\mathrm{Ni}]_T$ [a] M	$10^4[\mathrm{HO_2C{\cdot}CHR{\cdot}CO_2H}]_T$ [a] M	$10^4[\mathrm{H^+}]$ M	Indicator	10^4A M	$10^4\tau_{obs}$ s	$10^4\tau_{calc}$ s
Methylmalonic acid						
70·0	30·0	0·0196	*b*	83·5	18	17
60·0	30·0	0·0283	*b*	76·1	19	18
50·0	20·0	0·0414	*b*	69·0	19	20
60·0	30·0	0·0635	*b*	76·2	18	18
70·0	30·0	0·0939	*b*	84·1	16	15
60·0	30·0	0·165	*c*	74·2	16	16
50·0	20·0	0·223	*c*	63·7	15	17
60·0	30·0	0·271	*c*	69·3	16	15
80·0	40·0	0·300	*c*	82·0	12	12
60·0	40·0	0·326	*c*	67·3	15	14
80·0	40·0	0·365	*c*	78·1	12	12
80·0	40·0	0·419	*c*	74·7	12	12
60·0	40·0	0·528	*c*	57·9	14	14
82·0	40·7	0·712	*c*	59·8	13	12
70·0	40·0	0·837	*c*	50·3	14	13
90·0	60·0	1·07	*d*	51·1	11	11
60·0	50·0	1·21	*d*	39·7	14	14
60·0	50·0	1·33	*d*	38·0	12	14
60·0	50·0	1·56	*d*	35·4	13	13
90·0	70·0	1·87	*d*	37·9	11	11
70·0	60·0	2·14	*d*	33·1	12	12
100	70·0	2·50	*d*	34·5	11	10
100	80·0	2·68	*d*	33·8	10	10
90·0	70·0	3·11	*d*	31·0	12	10
120	100	3·37	*d*	32·9	8·7	9·2
120	100	3·53	*d*	32·3	9·0	9·2
90·0	70·0	3·78	*d*	29·3	9·8	9·8
120	100	4·24	*d*	30·5	8·5	8·8
120	100	4·70	*d*	29·6	8·6	8·6
120	90·0	5·10	*d*	28·9	8·8	8·5
n-Butylmalonic acid						
50·0	30·0	0·0233	*b*	79·7	17	17
50·0	30·0	0·0374	*b*	79·3	16	17
60·0	40·0	0·0818	*b*	86·6	15	14
60·0	40·0	0·161	*c*	84·6	13	13
50·0	40·0	0·230	*c*	74·1	13	14
80·0	40·0	0·244	*c*	95·5	12	11
50·0	50·0	0·290	*c*	72·0	13	13
60·0	40·0	0·341	*c*	75·6	13	12
60·0	50·0	0·410	*c*	73·0	12	12
60·0	60·0	0·712	*c*	60·3	11	11
80·0	60·0	0·917	*d*	60·4	9·6	10
80·0	60·0	1·01	*d*	57·5	10	10
90·0	60·0	1·25	*d*	53·9	9·5	9·4
80·0	70·0	1·67	*d*	46·0	9·5	9·3
100	80·0	1·92	*d*	46·4	8·4	8·5
80·0	70·0	2·20	*d*	41·5	9·0	8·8
100	80·0	2·25	*d*	43·6	8·9	8·2
100	80·0	2·41	*d*	42·6	8·2	8·1
122	100	2·62	*d*	43·7	7·1	7·5
90·0	80·0	2·64	*d*	40·4	7·9	8·1
100	80·0	2·71	*d*	40·9	8·5	7·8
122	100	2·87	*d*	42·4	7·6	7·3
122	100	2·88	*d*	42·2	7·2	7·3
120	100	3·18	*d*	41·0	7·7	7·1
90·0	80·0	3·25	*d*	38·3	7·1	7·5
90·0	90·0	3·65	*d*	37·5	7·8	7·1
122	100	3·65	*d*	39·4	6·7	6·8
120	100	3·74	*d*	39·1	7·1	6·8
122	100	3·84	*d*	38·9	6·2	6·7
120	100	4·12	*d*	38·2	6·6	6·5
90·0	90·0	4·19	*d*	36·6	7·3	6·8
122	100	4·39	*d*	37·7	6·0	6·4
120	100	4·44	*d*	37·6	6·2	6·4
120	100	4·54	*d*	37·3	6·4	6·3
122	100	4·81	*d*	37·1	6·9	6·2
120	100	4·87	*d*	36·9	6·0	6·1
120	100	5·40	*d*	36·2	5·8	5·9

[a] Total molar concentration. [b] Chlorophenol Red. [c] Bromocresol Green. [d] Bromochlorophenol Blue.

brackets indicate equilibrium concentrations. Since the quantity N is negligible compared to A under the conditions of the experiments, expression (11) can be rewritten as shown in (18), where the constants a, b, and c

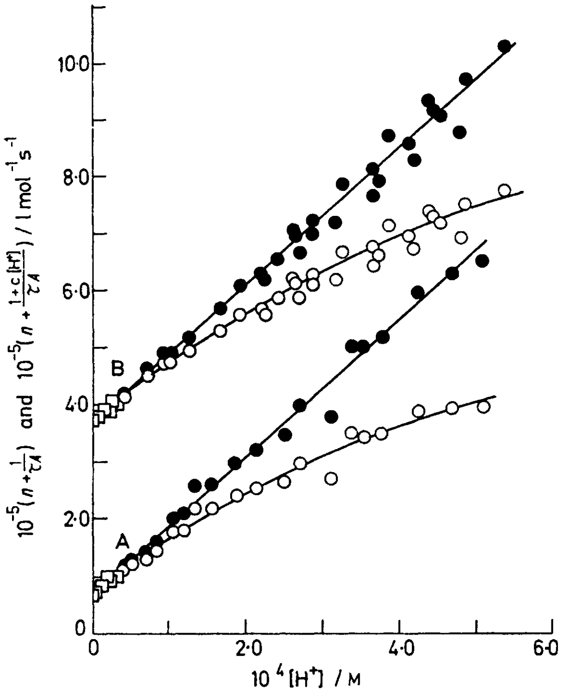
$$1/\tau A = (a + b[\mathrm{H}^+])/(1 + c[\mathrm{H}^+]) \tag{18}$$

$$a = k_1k_2K_0/(k_{-1} + k_2) \tag{19}$$

$$b = k_1'k_{\mathrm{H}}k_2K_0'/K_2^{\mathrm{H}}(k_{-1}' + k_{\mathrm{H}})(k_{-1} + k_2) \tag{20}$$

$$c = k_{-1}'k_{-\mathrm{H}}/(k_{-1}' + k_{\mathrm{H}})(k_{-1} + k_2) \tag{21}$$

are given by equations (19)—(21). Expression (18) is more general than that reported previously [2,3] for nickel and cobalt monomalonate complex formation (the quantity N is also negligible compared to A).



Plots of $1/\tau A$ (○) and $(1 + c[\mathrm{H}^+])/\tau A$ (●) against the hydrogen-ion concentration for: A, methylmalonic acid, $n = 0$; B, n-butylmalonic acid, $n = 3$; (□) common points. Some experimental points at lower acidities have been omitted

The Figure shows that a plot of $1/\tau A$ against the hydrogen-ion concentration yields a curve for both ligands examined; $1/\tau A$ increases less rapidly than as required for direct proportionality to $[\mathrm{H}^+]$ in accordance with the derived equation (18) and, consequently, with the reaction mechanism proposed. Values of the constants a, b, and c, obtained for each ligand from the curve (see Figure) which gives a best fit of the experimental data, are reported in Table 3. The uncertainty in the a values is *ca.* ±10%, whereas that in b and c is *ca.* ±15%.

In order to test the reliability of the calculated values of the constants a, b, and c, and to verify further the validity of equation (18), we have plotted the quantity $(1 + c(\mathrm{H}^+])/\tau A$ against $[\mathrm{H}^+]$ using the c values given in Table 3. The plots in the Figure show that $(1 + c[\mathrm{H}^+])/\tau A$ is a linear function of $[\mathrm{H}^+]$ for both ligands over the whole acidity range covered, as predicted from equation (18). Moreover the values of the intercept and slope of the straight lines obtained (see Figure; the correlation coefficients are **0·996** and **0·994** for the methyl- and n-butyl-malonic acids respectively) are in excellent agreement with those of a and b reported in Table **3**. The constants a, b, and c have also been used to calculate the relaxation times for the various solutions examined and the agreement between observed and calculated τ values (Table 2) is very satisfactory.

TABLE 3

Rate and equilibrium constants for the various steps involved in the formation of nickel(II) monochelate complexes with methyl- and n-butyl-malonic acids ($I = 0{\cdot}10$M; $t = 25$ °C)

	Methyl-malonic acid	n-Butyl-malonic acid
$10^{-4}a$/l mol^{-1} s^{-1}	6·8	7·1
$10^{-9}b$/l^2 mol^{-2} s^{-1}	1·2	1·2
$10^{-3}c$/l mol^{-1}	1·3	1·0
$10^{-3}bK_2^{\mathrm{H}}$/l mol^{-1} s^{-1}	4·8	3·8
$k_2/(k_{-1} + k_2)$	0·93	0·94
k_2/k_{-1}	13	16
$10^{-4}k_1K_0$/l mol^{-1} s^{-1}	7·3	7·5
$10^{-3}k_1'k_{\mathrm{H}}K_0'/(k_{-1}' + k_{\mathrm{H}})$ $10^{-3}k_1'K_0'$ * } /l mol^{-1} s^{-1}	5·1	4·0
$10^{-3}k_{-2}$/s^{-1}	2·2	3·9
$10^{-2}k_{-1}/K_2$(s^{-1})	1·7	2·4
$10^{-6}k_{-1}'k_{-\mathrm{H}}/K_2(k_{-1}' + k_{\mathrm{H}})$ $10^{-6}k_{-1}'/K_2K_{\mathrm{H}}$ * } /l mol^{-1} s^{-1}	3·1	4·1
$10^{-3}k_{-1}$/s^{-1}	3·3	3·1
$10^{-4}k_{-1}'$/s^{-1}	1·3	1·4
$10^{-4}k_2$/s^{-1}	4·2	5·1
K_2	19	13
10^4K_{H}/mol l^{-1}	2·2	2·6
K_0K_1/l mol^{-1}	22	24
$K_0'K_1'$/l mol^{-1}	0·40	0·29

* Assuming $k_{\mathrm{H}} > k_{-1}'$ (see text).

Having estimated constants a, b, and c, it is now possible to evaluate all the kinetic quantities given in relations (22)—(27) by combining equations (19)—(21)

$$1 - ac/b = k_2/(k_{-1} + k_2);\ a/(1 - ac/b) = k_1K_0 \tag{22}$$

$$b/ac - 1 = k_2/k_{-1} \tag{23}$$

$$b/cK_{\mathrm{C}} = k_{-2} \tag{24}$$

$$bK_2^{\mathrm{H}}/(1 - ac/b) = k_1'k_{\mathrm{H}}K_0'/(k_{-1}' + k_{\mathrm{H}}) \tag{25}$$

$$a/K_{\mathrm{C}}(1 - ac/b) = k_{-1}/K_2 \tag{26}$$

$$b/K_{\mathrm{C}}(1 - ac/b) = k_{-1}'k_{-\mathrm{H}}/K_2(k_{-1}' + k_{\mathrm{H}}) \tag{27}$$

with $K_{\mathrm{C}} = k_1k_2K_0/k_{-1}k_{-2}$ and $K_{\mathrm{C}}K_2^{\mathrm{H}} = k_1'k_{\mathrm{H}}k_2K_0'/k_{-1}'k_{-\mathrm{H}}k_{-2}$. The values obtained for these quantities are also reported in Table **3**.

An interesting result of the present work is the evaluation of k_2/k_{-1} [equation (23)] which allows us to establish the contribution of ring closure to the limiting rate in the overall chelate-formation process. It can be seen from Table **3** that, for both ligands, the rate constant (k_2) for ring closure is larger by a factor of **13**—**16** than that (k_{-1}) for dissociation of the monodentate complex

$(H_2O)_5Ni(O_2C{\cdot}CHR{\cdot}CO_2)$. It is then deduced that, when the term $c[H^+]$ is negligible with respect to unity (*i.e.* at acidities less than *ca.* 10^{-4}M), the chelate ring closure contributes negligibly to the rate-limiting process. This conclusion, of course, can also be drawn by considering the $k_2/(k_{-1} + k_2)$ values which are not very different from unity, or by comparing values of k_1K_0 and a, together with those of $k_1'k_HK_0'/(k_{-1}' + k_H)$ and bK_2^H; the differences in these values are within experimental error [*cf.* Table 3 and equations (19), (20), (22), and (25)]. The rate-determining step in the reaction of $Ni(H_2O)_6^{2+}$ with the dianionic ligand $O_2C{\cdot}CHR{\cdot}CO_2^{2-}$ is thus formation of the monodentate intermediate $(H_2O)_5Ni(O_2C{\cdot}CHR{\cdot}CO_2)$ [*cf.* equation (19)].

For the reaction between the metal ion and the monoanionic ligand $HO_2C{\cdot}CHR{\cdot}CO_2^-$, depending upon the relative magnitudes of k_{-1}' and k_H, the reaction rate may be determined [*cf.* equation (20) or (25)] either by formation of the acid intermediate complex $(H_2O)_5Ni(O_2C{\cdot}CHR{\cdot}CO_2H)^+$ (if $k_H > k_{-1}'$), or by the proton-transfer process (9) (if $k_H < k_{-1}'$). Since proton-transfer reactions are normally fast, assuming $k_H > k_{-1}'$, the quantity $k_1'k_HK_0'/(k_{-1}' + k_H)$ reduces to $k_1'K_0'$ and formation of the acid intermediate [reaction (8)] is the rate-determining step. Bearing in mind that the outer-sphere association constant K_0 has to be greater [2-4,15] than K_0', the difference of only one order of magnitude (see Table 3) in the values of k_1K_0 and $k_1'K_0'$ [or $k_1'k_HK_0'/(k_{-1}' + k_H)$] lends support to the assumption made (*i.e.* $k_H > k_{-1}'$). In fact, much larger differences in the overall rates of reactions involving an unprotonated ligand and the corresponding monoprotonated form are found when proton release is a relatively slow process.[16]

Since nickel complex formation reactions classified as 'normal' appear to occur [4,5] by a dissociative mechanism (see Introduction), we can conclude that the reactions of the nickel(II) ion with the two reacting forms of the ligands examined are controlled by loss of the first water molecule from the inner co-ordination sphere of the metal ion.

It should be pointed out that if the contribution of the reaction involving the neutral form of the ligand $(HO_2C{\cdot}CHR{\cdot}CO_2H)$ was always negligible and equation (18) valid over an acidity range wider than that studied, the quantity $1/\tau A$ would become independent of $[H^+]$ and equal to $b/c = k_2K_0'K_1'K_H/K_2^H$ at acidities greater than *ca.* 10^{-2}M. As a consequence of this the reaction of nickel(II) with the monoanion $HO_2C{\cdot}CHR{\cdot}CO_2^-$ would be determined by the ring-closure process [reaction (10)].

Considering in particular now the reaction involving the dianion $O_2C{\cdot}CHR{\cdot}CO_2^{2-}$, it is apparent from Table 3 that the chain length of the alkyl groups has no effect on the values of a and of k_1K_0 and, hence, the reaction mechanism. Since the k_1K_0 values of the present work are equal to that ($7{\cdot}0 \times 10^4$ l mol^{-1} s^{-1} at 25 °C and $I = 0{\cdot}1$M) found previously [2] for the malonate anion by assuming $k_2 > k_{-1}$, it is reasonable to deduce that the previous assumption is correct and, consequently, that for the nickel(II)–malonate system also ring closure does not contribute significantly to the overall rate of chelate formation.

This conclusion is further supported by the following considerations. Because for the nickel(II)–malonate system $1/\tau A$ was found [2] to be a linear function of the hydrogen-ion concentration over the acidity range investigated (at 25 °C: $1{\cdot}90 \times 10^{-5}\text{M} \leqslant [H^+] \leqslant 4{\cdot}09 \times 10^{-4}\text{M}$), according to expression (18), the term $c[H^+]$ has to be negligible compared to unity. Assuming $c[H^+] \leqslant 0{\cdot}1$ (*i.e.* 10% of unity) at the higher hydrogen-ion concentration studied, it can be calculated that $c \leqslant 2{\cdot}4 \times 10^2$ l mol^{-1}. Moreover, using the values of the intercept ($a = 7{\cdot}0 \times 10^4$ l mol^{-1} s^{-1}) and slope ($b = 5{\cdot}5 \times 10^8$ l^2 mol^{-2} s^{-1}) obtained [2] at 25 °C from the $1/\tau A$ against $[H^+]$ plot, it is possible to see, by application of equation (23), that $k_2/k_{-1} \geqslant 32$. Thus we find, once again, that for the nickel(II)–malonate system the ring closure process is faster than dissociation of the monodentate intermediate $(H_2O)_5Ni(O_2C{\cdot}CH_2{\cdot}CO_2)$. This result is in contrast with that deduced for the same system by Hoffmann,[6] who estimated (see Introduction) that $k_2 \approx k_{-1}$. On the basis of the above considerations, Hoffmann's assumption that the rate constant k_1K_0 for the malonate anion can be equated to that for the adipate anion, does not seem to be reliable. It should be pointed out that, making allowance for temperature and/or ionic strength, the value of $7{\cdot}0 \times 10^4$ l mol^{-1} s^{-1} found at 25 °C and $I = 0{\cdot}1$M for the rate constant for the present reaction is in good agreement [6,17] with those determined by Bear and Lin ($2{\cdot}7 \times 10^5$ l mol^{-1} s^{-1} at 20 °C and $I = 0$) and by Hoffmann, Stuehr, and Yeager ($4{\cdot}2 \times 10^5$ l mol^{-1} s^{-1} at 25 °C and $I = 0$) with the pressure-jump method.

According to equation (24), the kinetic data of the present work also permit evaluation of the rate constant (k_{-2}) for opening of the chelate ring. As Table 3 shows, the value for the n-butylmalonate anion is slightly larger than that obtained for the methyl derivative. Although the difference is small, it seems there is some effect of the alkyl groups on the rate of chelate ring opening. A comparison with the k_{-2} value estimated by Hoffmann [6] for the unsubstituted malonate anion cannot be made for the reasons discussed above.

Bearing in mind that $k_H > k_{-1}'$, $K_C = K_0K_1K_2$, and $K_CK_2^H = K_0'K_1'K_HK_2$, it would be possible to evaluate the rate constant k_2 ($= k_{-2}K_2$) and all the stepwise equilibrium constants K_2 [equation (26)], K_H [equation (27)], K_0K_1, and $K_0'K_1'$ if the rate constants k_{-1} and k_{-1}' were known. Hoffmann and Yeager [6,18] have observed

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that, for a series of mono-complexes of nickel(II) with carboxylic acids, the dissociation rate constant is proportional to the basicity of the co-ordinated carboxylate group. Using this observation, values to k_{-1} and to k_{-1}' can be assigned, the basicities of the co-ordinated carboxylate groups being given in the present case by pK_2^H and pK_1^H respectively. Since data at zero ionic strength were used by Hoffmann and Yeager, the k_{-1} and k_{-1}' values have been interpolated by utilizing pK_2^H and pK_1^H at $I = 0$. The values of these rate constants together with those of k_2 and of all the stepwise equilibrium constants are given in Table 3.

The similarity of the rate constants k_2 for the two ligands examined indicates that the length of the alkyl group has practically no effect upon the ring-closure rate. Moreover these rate constants are smaller by only a factor of *ca.* 2 than those (k_1K_0) for formation of the monodentate complex $(H_2O)_5Ni(O_2C{\cdot}CHR{\cdot}CO_2)$ and similar to the water-exchange rate constant.[19] On the other hand, they are larger than those for formation of the acid intermediate $(H_2O)_5Ni(O_2C{\cdot}CHR{\cdot}CO_2H)^+$, which involves the univalent reacting anion $CO_2C{\cdot}CHR{\cdot}CO_2^-$. Therefore, bearing also in mind that the presence of a carboxylate group in the inner co-ordination sphere of a metal ion appears to have practically no labilizing effect [4a, 20] on the other co-ordinated ligands (*e.g.* water), it seems there is no significant difficulty in closing the six-membered chelate ring.

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