Relaxation Kinetic Study of Monophthalatonickel(II) Complex Formation

By **Francesco P. Cavasino,* Emanuele Di Dio,** and **Giovanni Locanto,** Istituto di Chimica Fisica, Università, 90123 Palermo, Italy

The temperature-jump relaxation method has been used to study the kinetics of the reaction between nickel(II) ion and phthalic acid in aqueous solution, at 25 °C and ionic strength 0·10M, over the acidity range from 2×10^{-6} to 4×10^{-4}M. The observed pH dependence of the overall rate of complex formation suggests that the nickel(II) ion reacts with both the dianionic and monoanionic species of the dicarboxylic acid and that the phthalate anion acts as a bidentate ligand, forming a seven-membered chelate ring with the metal ion. The kinetic results show, moreover, that chelate-ring closure contributes to some extent to the limiting rate in the overall chelation process and that the rate of chelate-ring opening is faster for phthalate anion than for methyl- and n-butyl-malonate, *i.e.* the larger chelate ring is easier to open than the smaller one.

THE previous study [1] on the kinetics of reaction of the nickel(II) ion with methyl- and n-butyl-malonic acids in aqueous solution showed that two reactions contribute significantly to formation of the nickel(II) monochelate complex over the acidity range investigated ($2 \times 10^{-6}\text{M} \leqslant [\text{H}^+] \leqslant 5 \times 10^{-4}\text{M}$), *i.e.* the reactions of the nickel(II) ion with both the dianionic and monoanionic forms of the dicarboxylic acids. The existence of these two competitive reaction paths allowed us to establish that closure of the six-membered chelate ring is faster than 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) and that ring closure does not contribute significantly to the limiting rate in the overall chelate-formation process. Similar conclusions were also drawn by a different indirect approach for monomalonatonickel(II) complex formation.[1,2]

Continuing our researches on the influence of the structure of the ligand on the kinetics and mechanism of metal chelate-complex formation, we have studied, by the temperature-jump method, the kinetics of formation of the monophthalatonickel(II) complex, in aqueous solution at 25 °C and ionic strength I = 0·10M, over the acidity range from 2×10^{-6} to 4×10^{-4}M. According to stability studies,[3,4] the phthalate anion is considered to form a seven-membered chelate ring with nickel(II) ion. On the other hand, it seems kinetically [5,6] that dicarboxylate anions which might also form seven-membered rings (*i.e.* succinate and maleate anions) act as unidentate rather than as bidentate ligands. Therefore this study was of particular interest in view of the fact that the chelating nature of phthalic acid could be established kinetically if a pH dependence of the overall rate of complex formation, analogous to that previously [1] found for nickel(II) methyl- and n-butyl-malonato-complexes, was observed.

EXPERIMENTAL

Phthalic acid (Fluka, reagent grade) was used without further purification. The other substances were those used previously.[1] Stock solutions of nickel(II) perchlorate, sodium perchlorate, phthalic acid, and indicators (Chlorophenol Red, Bromocresol Green, and Bromochlorophenol Blue) were prepared as described before.[1] The indicators were used to follow the course of the relaxation process. Kinetic measurements were performed at 25 °C and ionic strength 0·10M (supporting electrolyte $NaClO_4$). The apparatus, experimental procedure, and methods employed for evaluation of the relaxation times and the hydrogen-ion concentrations, were those described previously.[1]

All the solutions exhibited a relaxation spectrum characterized by a single relaxation time. Blank experiments did not show any discernible relaxation effect. The evaluated relaxation times 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

The reaction mechanism proposed previously [1,2] for the formation of nickel(II) monochelate complexes with malonic acid and its methyl- and n-butyl-derivatives fits well the complete range of experimental kinetic data for the present work. This mechanism is presented below for phthalic acid ($HO_2C{\cdot}C_6H_4{\cdot}CO_2H$). Here $(H_2O)_6Ni,O_2C{\cdot}C_6H_4{\cdot}CO_2$ and $(H_2O)_6Ni,O_2C{\cdot}C_6H_4{\cdot}CO_2H^+$ represent outer-sphere complexes [reactions (1) and (2)] and $[(H_2O)_5Ni(O_2C{\cdot}C_6H_4{\cdot}CO_2)]$ and $[(H_2O)_5Ni(O_2C{\cdot}C_6H_4{\cdot}CO_2H)]^+$ monodentate complexes [reactions (3) and (4)]. Moreover, reaction (5) is to be considered a proton-transfer process involving, probably, the solvent as proton acceptor. According to this mechanism and assuming that the protolytic reactions (7)—(9) relative to the dissociation of the acid ligand and of the indicator added (HIn) are very rapid and in equilibrium at all times, the previously [1] derived expression for the relaxation time τ, valid under the experimental conditions of the present work, is given

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[1] G. Calvaruso, F. P. Cavasino, and E. Di Dio, *J.C.S. Dalton*, 1972, 2632.

[2] F. P. Cavasino, *J. Phys. Chem.*, 1965, **69**, 4380.

[3] M. Yasuda, K. Suzuki, and K. Yamasaki, *J. Phys. Chem.*, 1956, **60**, 1649.

[4] I. R. Desai and V. S. K. Nair, *J. Chem. Soc.*, 1962, 2360.

[5] H. Hoffmann and E. Yeager, quoted in ref. 6.

[6] H. Hoffmann and U. Nickel, *Ber. Bunsengesellschaft Phys. Chem.*, 1968, **72**, 1096; H. Hoffmann, *ibid.*, 1969, **73**, 432.

in equation (10) [where *a*, *b*, *c*, and *A* are given by equations (11)—(14) (the square brackets represent equili-

$$O_2C{\cdot}C_6H_4{\cdot}CO_2^{2-} \underset{\text{v. fast}}{\overset{K_0}{\rightleftharpoons}} (H_2O)_6Ni,O_2C{\cdot}C_6H_4{\cdot}CO_2 \quad (1)$$

$$[Ni(H_2O)_6^{2+}] + \quad -H^+ \uparrow\downarrow + H^+$$

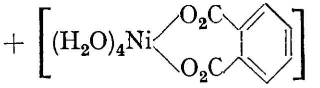
$$HO_2C{\cdot}C_6H_4{\cdot}CO_2^- \underset{\text{v. fast}}{\overset{K_0'}{\rightleftharpoons}} (H_2O)_6Ni,O_2C{\cdot}C_6H_4{\cdot}CO_2H^+ \quad (2)$$

$$(H_2O)_6Ni,O_2C{\cdot}C_6H_4{\cdot}CO_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_2O + [(H_2O)_5Ni(O_2C{\cdot}C_6H_4{\cdot}CO_2)] \quad K_1 = k_1/k_{-1} \quad (3)$$

$$(H_2O)_6Ni,O_2C{\cdot}C_6H_4{\cdot}CO_2H^+ \underset{k_{-1}'}{\overset{k_1'}{\rightleftharpoons}} H_2O + [(H_2O)_5Ni(O_2C{\cdot}C_6H_4{\cdot}CO_2H)]^+ \quad K_1' = k_1'/k_{-1}' \quad (4)$$

$$[(H_2O)_5Ni(O_2C{\cdot}C_6H_4{\cdot}CO_2H)]^+ \underset{k_{-H}}{\overset{k_H}{\rightleftharpoons}} H^+ + [(H_2O)_5Ni(O_2C{\cdot}C_6H_4{\cdot}CO_2)] \quad K_H = k_H/k_{-H} \quad (5)$$

$$[(H_2O)_5Ni(O_2C{\cdot}C_6H_4{\cdot}CO_2)] \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} H_2O +$$



$$K_2 = k_2/k_{-2} \quad (6)$$

brium concentrations), α and β are quantities [1,2] depending on equilibrium constants and equilibrium concen-

$$HO_2C{\cdot}C_6H_4{\cdot}CO_2H \overset{K_1{}^H}{\rightleftharpoons} HO_2C{\cdot}C_6H_4{\cdot}CO_2^- + H^+ \quad (7)$$

$$HO_2C{\cdot}C_6H_4{\cdot}CO_2^- \overset{K_2{}^H}{\rightleftharpoons} O_2C{\cdot}C_6H_4{\cdot}CO_2^{2-} + H^+ \quad (8)$$

$$HIn \overset{K_i}{\rightleftharpoons} In^- + H^+ \quad (9)$$

trations of the chemical species in reactions (7)—(9), and K_C is the equilibrium constant for reaction (15)].

$$1/\tau A = (a + b[H^+])/(1 + c[H^+]) \quad (10)$$

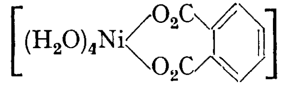
$$a = k_1k_2K_0/(k_{-1} + k_2) \quad (11)$$

$$b = k_1'k_Hk_2K_0'/K_2{}^H(k_{-1}' + k_H)(k_{-1} + k_2) \quad (12)$$

$$c = k_{-1}'k_{-H}/(k_{-1}' + k_H)(k_{-1} + k_2) \quad (13)$$

$$A = \{[Ni^{2+}]/(1 + \alpha + \beta)\} + [O_2C{\cdot}C_6H_4{\cdot}CO_2^{2-}] + (1/K_C) \quad (14)$$

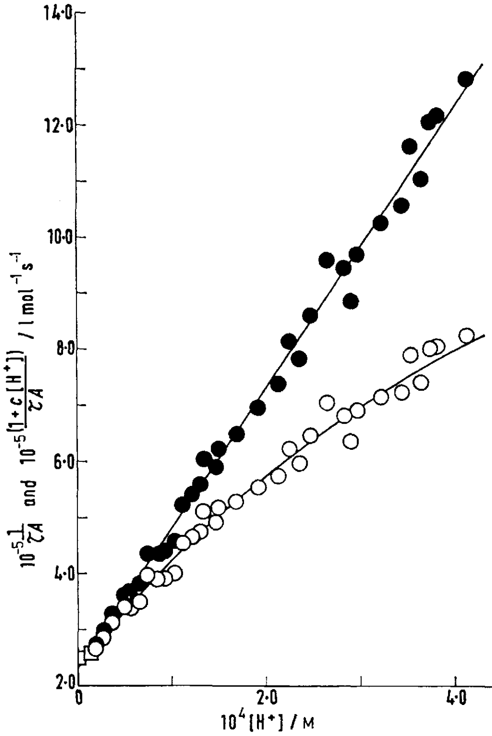
$$[Ni(H_2O)_6^{2+}] + O_2C{\cdot}C_6H_4{\cdot}CO_2^{2-} \overset{K_C}{\rightleftharpoons} 2H_2O +$$



$$(15)$$

The experimental conditions and the pertinent equilibrium constants used in the present work are reported in Table 1 together with the calculated *A* values [equation (14)] and the observed relaxation times. It is apparent from the Figure that a curve is obtained when $1/\tau A$ is plotted against the hydrogen-ion concentration as predicted from equation (10) and, hence, from the above reaction mechanism. The constants *a*, *b*, and *c*, obtained from the curve (see Figure) which gives a best fit of the experimental data, are equal to $2{\cdot}3 \times 10^5$ l mol^{-1} s^{-1}, $2{\cdot}5 \times 10^9$ l^2 mol^{-2} s^{-1}, and $1{\cdot}3_5 \times 10^3$ l mol^{-1}, respectively. Since $1/\tau A$ reduces to *a* as [H$^+$] approaches zero, the uncertainty in the constant *a* can be considered equal to the maximum uncertainty in the $1/\tau A$ values, which in effect is that in the relaxation times (*i.e.*, *ca.* ±10%; *cf.* Experimental section). The uncertainty in both the constants *b* and *c* is *ca.* ±15% and has been estimated by considering the worse curves drawn by taking into account the uncertainties in all the $1/\tau A$ values.

It should be pointed out that use of the equilibrium constants obtained by Desai and Nair [4] at $I = 0$ and corrected at ionic strength 0·10M using the Davies equation [4] leads, within the limits of the estimated uncertainties, to the values of *a*, *b*, and *c* given above. If the obtained *c* value is used, a plot of $(1 + c[H^+])/\tau A$ against [H$^+$] yields a straight line [*cf.* equation (10) and the Figure; the correlation coefficient is 0·996] having intercept and gradient respectively equal to the *a* and *b* values reported. Moreover, relaxation times calculated using the constants *a*, *b*, and *c*, by means of equation (10), are in good agreement with those observed (*cf.* Table 1).



Plots of $1/\tau A$ (○) and $(1 + c[H^+])/\tau A$ (●) against hydrogen-ion concentration; (□) common points

These facts lend strong support to the suggestion that formation of the monophthalatonickel(II) complex occurs by the same mechanism proposed [1,2] for the corresponding reactions with the malonic acid derivatives and, consequently, that phthalic acid acts as a bidentate ligand forming a seven-membered chelate ring with the nickel(II) ion. It is to be noted that the chelating nature of phthalic acid would have remained doubtful if the $1/\tau A$ against $[H^+]$ plot had been linear. In fact, a linear plot would be expected both in the case of formation of a chelate ring when $c[H^+] < 1$ [*cf.* equation (10)], and in the case in which phthalic acid acts as a unidentate ligand and reaction (6) does not occur.

TABLE 1

Experimental conditions, pertinent equilibrium constants,[a–d] and relaxation times ($I = 0{\cdot}10$M; $t = 25$ °C) for the reaction of nickel(II) ion with phthalic acid

$10^4[\mathrm{Ni}]_T$ [e]	$10^4[HO_2C{\cdot}C_6H_4{\cdot}CO_2H]_T$ [f]	$10^4[H^+]$	HIn [g]	10^4A	$10^4\tau_{obs}$	$10^4\tau_{calc}$
M	M	M		M	s	s
60·0	30·0	0·0215	*b*	137	2·9	3·1
80·0	40·0	0·156	*c*	151	2·6	2·5
80·0	40·0	0·196	*c*	150	2·5	2·4
70·0	40·0	0·277	*c*	140	2·5	2·5
70·0	40·0	0·365	*c*	139	2·3	2·3
70·0	50·0	0·504	*c*	134	2·2	2·2
80·0	50·0	0·565	*c*	140	2·1	2·1
80·0	50·0	0·672	*c*	136	2·1	2·0
80·0	50·0	0·745	*c*	133	1·9	2·0
80·0	50·0	0·876	*d*	129	2·0	1·9
80·0	60·0	0·938	*d*	128	2·0	1·9
80·0	60·0	1·04	*d*	125	2·0	1·9
80·0	60·0	1·12	*d*	122	1·8	1·8
80·0	60·0	1·22	*d*	119	1·8	1·8
80·0	60·0	1·31	*d*	117	1·8	1·8
80·0	50·0	1·34	*d*	115	1·7	1·8
80·0	60·0	1·47	*d*	113	1·8	1·8
80·0	70·0	1·49	*d*	114	1·7	1·7
100	80·0	1·69	*d*	118	1·6	1·6
100	80·0	1·92	*d*	113	1·6	1·6
100	80·0	2·13	*d*	109	1·6	1·5
100	80·0	2·25	*d*	107	1·5	1·5
100	80·0	2·36	*d*	105	1·6	1·5
98·4	80·0	2·47	*d*	103	1·5	1·5
100	80·0	2·65	*d*	101	1·4	1·5
120	90·0	2·83	*d*	105	1·4	1·4
122	100	2·90	*d*	105	1·5	1·4
120	100	2·97	*d*	103	1·4	1·4
120	90·0	3·22	*d*	100	1·4	1·4
122	100	3·44	*d*	98·9	1·4	1·4
120	100	3·53	*d*	97·8	1·3	1·4
120	100	3·65	*d*	96·7	1·4	1·3
120	100	3·74	*d*	96·0	1·3	1·3
122	100	3·81	*d*	95·8	1·3	1·3
122	100	4·14	*d*	93·5	1·3	1·3

[a] $K_C = 138$ l mol^{-1}, $K_1^H = 1{\cdot}74 \times 10^{-3}$ mol l^{-1}, and $K_2^H = 1{\cdot}20 \times 10^{-5}$ mol l^{-1} (ref. 3). [b] Chlorophenol Red, $K_i = 1{\cdot}1 \times 10^{-6}$ mol l^{-1} (ref. 1). [c] Bromocresol Green, $K_i = 2{\cdot}0 \times 10^{-5}$ mol l^{-1} (ref. 1). [d] Bromochlorophenol Blue, $K_i = 1{\cdot}0 \times 10^{-4}$ mol l^{-1} (ref. 1). [e] Total molar concentration of nickel(II) perchlorate. [f] Total molar concentration of phthalic acid. [g] Indicator.

In order to evaluate the rate constants, expressions (11)—(13) are combined[1] with $K_C = k_1k_2K_0/k_{-1}k_{-2}$ and $K_CK_2^H = k_1'k_Hk_2K_0'/k_{-1}'k_{-H}k_{-2}$ to give equations (16)—(21). Estimated values of the kinetic quantities and corresponding probable errors[7] are assembled in Table 2,

$$(b/ac) - 1 = k_2/k_{-1};\ 1 - (ac/b) = k_2(k_{-1} + k_2) \quad (16)$$

$$a/[1 - (ac/b)] = k_1K_0 \quad (17)$$

$$bK_2^H/[1 - (ac/b)] = k_1'k_HK_0'/(k_{-1}' + k_H) \quad (18)$$

$$b/cK_C = k_{-2} \quad (19)$$

$$a/K_C[1 - (ac/b)] = k_{-1}/K_2 \quad (20)$$

$$b/K_C[1 - (ac/b)] = k_{-1}'k_{-H}/K_2(k_{-1}' + k_H) \quad (21)$$

together with those found[1] for methyl- and n-butylmalonic acids. The probable errors were calculated[7] by considering the uncertainties in values of a, b, and c[1] and in those of K_2^H and K_C. Uncertainties in the latter values are known only for the nickel(II)–n-butylmalonate system[8] (*ca.* ±3%). However, the lack of known uncertainties in the equilibrium constants for the other two systems is not serious, since the probable errors in the kinetic quantities of equations (18—21) are not significantly affected by uncertainties of up to ±15%. Therefore the probable errors reported for these two systems have been obtained by assuming that the equilibrium constants K_2^H and K_C are affected by a maximum arbitrary error of ±10%.

Values obtained in the present work for k_2/k_{-1} and $k_2/(k_{-1} + k_2)$ indicate that, although chelate-ring closure is faster than dissociation of the monodentate complex $[(H_2O)_5Ni(O_2C{\cdot}C_6H_4{\cdot}CO_2)]$, it contributes to some extent to the limiting rate in the overall chelate-formation process. In the case of the monosubstituted malonic

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[7] H. Margenau and G. M. Murphy, 'The Mathematics of Physics and Chemistry,' 2nd edn., D. Van Nostrand Co., Princeton, 1962, p. 515.

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acids, the contribution of the ring-closure rate was less significant and practically negligible[1] (*cf.* Table 2).

The quantity k_1K_0 for the reaction of nickel(II) with the anion $O_2C{\cdot}C_6H_4{\cdot}CO_2^{2-}$ is greater by only a factor of *ca.* 8 than the quantity $k_1'k_HK_0'/(k_{-1}' + k_H)$ for the corresponding reaction with the anion $HO_2C{\cdot}C_6H_4{\cdot}CO_2^-$ (*cf.* Table 2). On the basis of electrostatics,[9] the outer-sphere association constant K_0 must be larger[1,2] than K_0'. Therefore, bearing also in mind that substitution of a unidentate ligand in the first co-ordination sphere of the aquonickel(II) ion is generally accepted[1,2,10] to occur by a dissociative mechanism and that, hence, in the present case, k_1 has to be similar to k_1', the values found for k_1K_0 and for $k_1'k_HK_0'/(k_{-1}' + k_H)$ lead to the conclusion that k_{-1}' is negligible compared to k_H and that $k_1'k_HK_0'/(k_{-1}' + k_H) = k_1'K_0'$. This result, which is analogous to that previously obtained[1] for the monosubstituted malonic acids, is also supported by the fact that much larger differences in rate are found for a given metal ion reacting with an unprotonated ligand and the corresponding monoprotonated species when the proton-transfer process is relatively slow.[1,11]

TABLE 2

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

	Mcthylmalonic acid	n-Butylmalonic acid	Phthalic acid
$k_2/(k_{-1} + k_2)$	0·93 ± 0·02	0·94 ± 0·02	0·88 ± 0·03
k_2/k_{-1}	13 ± 3	16 ± 4	7 ± 2
$10^{-4}k_1K_0$/l mol^{-1} s^{-1}	7·3 ± 0·8	7·5 ± 0·8	26 ± 3
$\left.\begin{matrix}10^{-3}k_1'k_HK_0'/(k_{-1}' + k_H)\\ 10^{-3}k_1'K_0'\ *\end{matrix}\right\}$ /l mol^{-1} s^{-1}	5·1 ± 0·9	4·0 ± 0·7	34 ± 6
$10^{-3}k_{-2}$/s^{-1}	2·2 ± 0·5	3·9 ± 0·9	13 ± 3
$10^{-2}(k_{-1}/K_2)$/s^{-1}	1·7 ± 0·3	2·4 ± 0·3	19 ± 3
$\left.\begin{matrix}10^{-6}k_{-1}'k_{-H}/K_2(k_{-1}' + k_H)\\ 10^{-6}k_{-1}'/K_2K_H\ *\end{matrix}\right\}$ /l mol^{-1} s^{-1}	3·1 ± 0·6	4·1 ± 0·7	21 ± 4

* With $k_H > k_{-1}'$ (see text).

Both the rate constants k_1K_0 and $k_1'K_0'$ are smaller for the malonic acid derivatives[1,2] than for phthalic acid (*cf.* Table 2). Since, as mentioned above, the same dissociative mechanism appears to be operative in formation of the monodentate intermediates, the observed different rates may be primarily ascribed to differences in the outer-sphere association constants. This is presumably a consequence of the different structure and flexibility of these ligands, which affects both the distance of closest approach of the two ion partners and the effective negative charge 'seen' from the cation in the outer-sphere complex.

With respect to the rate constant k_{-2}, Table 2 shows that the rate of chelate-ring opening increases in passing from the malonate anions (six-membered rings) to the phthalate anion (seven-membered ring). Therefore, the ring-opening rate is clearly dependent on ring size and, in particular, the larger chelate ring is easier to open than the smaller one.

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