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Kinetic Studies of the Nickel Phthalate Complex Formation in Solution by the Pressure-jump Method

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The rate constants of the complex formation and the dissociation of the nickel phthalate (*o*-phthalate) complex have been determined by the pressure-jump method. The thermodynamic parameters of the reaction were obtained from studies at various temperatures between 10 and 30 °C. Upon a comparison of the data on the nickel complexes of the succinate, adipate, maleate, and phthalate, no systematic relationship between the nature of the ligands and the kinetic values has been found; this can be ascribed to the monodentated form of these complexes. The rate-determining step is the loss of the water molecule from the inner-coordination sphere of the nickel ion when the monodentated complex is formed.

Although the equilibrium properties of the nickel dicarboxylate complexes[1] have been well studied, relatively few systematic kinetic studies have been carried out. The development of the relaxation techniques[2] has, however, made it possible to study these fast reactions kinetically. In many of these studies of the complex formation reactions, the relaxation effect has been ascribed to one of the reactions of the step-by-step mechanism proposed by Eigen *et al.*[2] When the nickel complex of the bidentate ligand is formed, two inner-coordinated waters should be replaced by the ligand. Therefore, the mechanism of the bidentated chelate complex formation through the outer-sphere complex and the monodentated complex has usually been proposed. If the complex is stable as a chelate, the rate-determining step can be discussed by two different theories. Nancollas and Sutin[3] and Cavasino[4] have thought that the first bond formation between the nickel ion and the ligand is the rate-determining step. On the other hand, Hoffmann *et al.*[5–8] have considered that the chelate-ring closure is the rate-determining step and have calculated the rate constants of each reaction of the step-by-step mechanism. Nevertheless, if the complex is stable as a monodentated form rather than as a chelate, the same treatment as that carried out in the nickel maleate complex formation[9] will be applied.

The present study was undertaken in an attempt to confirm if one of these theories can be applied to the nickel phthalate complex formation. Another purpose has been to ascertain the ligand effects on the kinetic values of the nickel dicarboxylate complexes where the ligand has a pair of the carboxylate group maintained by the C–C single bond, and the C–C double bond, and the aromatic ring.

Experimental

All of the chemicals used were of a reagent grade. The nickel phthalate solution was prepared by mixing a stoichiometric amount of $NiSO_4$ with phthalic acid. Titration with a solution of $Ba(OH)_2$ was done until all the sulfate ions had precipitated out as insoluble $BaSO_4$. The solid $BaSO_4$ was then removed by filtration. The titration of the solution to pH 6.5 yielded a solution with most of the ligands in the dissociated form. The concentration of the nickel phthalate was determined by dimethylglyoxime titration. The solution to be studied was prepared by the dilution of the standard solution to the desired concentration.

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The pressure-jump method with a conductivity readout has been described in considerable detail elsewhere.[10] The time constant of the apparatus was 100 μsec. A small improvement was made by placing a solenoid valve at the gas inlet of the pressure-jump cell. This improvement has resulted not only in making the experiments easier, but also in increasing the signal-to-noise ratio with the improvement of cutting off the entering of the useless gas after the metal diaphragm burst. Because of the use of the conductivity readout, no buffering or supporting electrolytes were added, and so the ionic strength of the solution was varied arbitrarily. In order to determine the kinetic parameters of the reaction, a series of experiments was run covering the concentration range from 0.00051 to 0.051 M of the nickel phthalate and the temperature range from 10 to 30 °C. The relaxation times quoted are the mean values of several runs.

Results

In all the nickel phthalate solutions, the relaxation spectrum was characterised by a single relaxation time. A representative relaxation spectrum is shown in Fig. 1. The experimental conditions and the observed relaxation times at 25 °C are shown in Table 1. In the present studies, the complex formation reaction may be expressed as follows:

$$M^{2+} + L^{2-} \underset{k_d}{\overset{k_f}{\rightleftharpoons}} ML \qquad (1)$$

where M^{2+} is the metal ion, L^{2-} is the ligand, ML is the complex, and k_f and k_d are the rate constants of the complex formation and the dissociation at zero ionic strength respectively. For such a mechanism, the rate constants are related to the relaxation time, τ, by the following equation:

$$1/\tau = k_f \gamma_\pm^2 (C_M + C_L) + k_d \qquad (2)$$

where $\gamma_\pm$ is the mean activity coefficient of the free ions at a finite ionic strength, and where C_M and C_L are the ionic concentrations of the metal ion and the ligand respectively. As may be seen from Eq. (2), the plot of $1/\tau$ against $\gamma_\pm^2(C_M+C_L)$ gives k_f and k_d from the slope and the intercept of the line respectively. Such a plot requires the stability constant, K $(=k_f/k_d)$, if we are to calculate the ionic concentrations. Unfortunately, however, an appropriate K was not available, so the values of k_f, k_d, and K were obtained in the following way.

As the first approximation, a value of K which had been estimated from the literature value[11] was used to calculate the ionic concentrations. The activity coefficients of the ions were calculated by the use of the Kielland equation.[12] Then, the $1/\tau$ values were plotted against $\gamma_\pm^2(C_M+C_L)$. Here, the ratio between

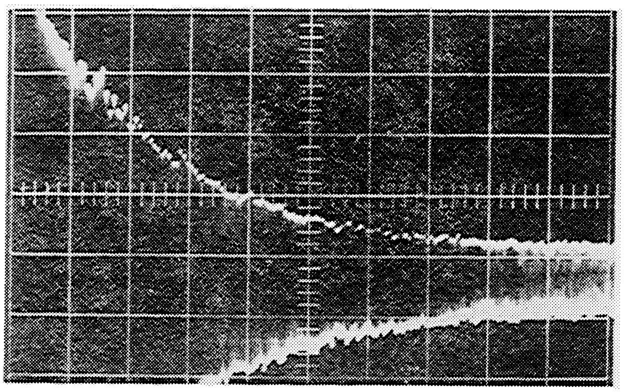

Fig. 1. Representative pressure-jump relaxation spectrum. 4.08×10^{-3} M Nickel phthalate; sweep 200 μsec/div. at 20°C.

Table 1. Relaxation times and experimental conditions for the nickel phthalate system at 25°C

C_0[a] (10^{-4} M)	C_{NiPh} (10^{-4} M)	$C_{Ni}=C_{Ph}$ (10^{-4} M)	μ (10^{-4})	$\gamma_\pm$	$1/\tau$ (10^3 sec^{-1})
5.1	0.6	4.6	18.4	0.83	3.1
10.2	1.7	8.5	34.0	0.78	3.3
20.4	5.4	15.0	60.0	0.73	3.6
40.8	15.4	25.4	102	0.68	4.2
61.2	27.4	33.8	135	0.64	4.4
102	54.4	47.6	190	0.60	4.8
204	130	73.7	295	0.55	5.3
306	212	94.0	376	0.52	5.7
408	297	111	445	0.50	6.1
510	384	126	506	0.48	6.4

a) C_0 refers to the total stoichiometric concentrations of the nickel phthalate.

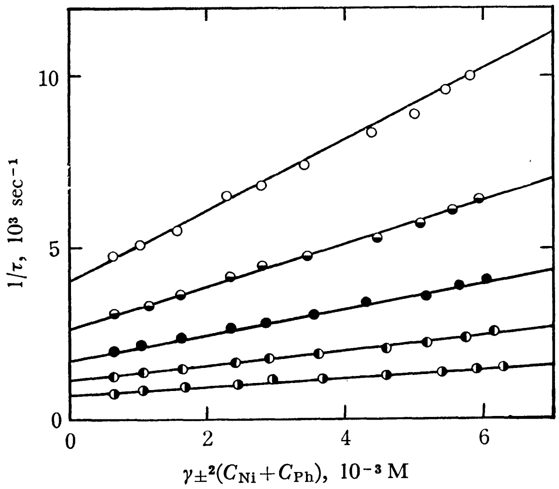

Fig. 2. $1/\tau$ vs. $\gamma_\pm^2(C_{Ni}+C_{Ph})$ plot at 10°C (◑), 15°C (◐), 20 °C (●), 25 °C (◒), and 30 °C (○).

Table 2. The formation and dissociation rate constants and the stability constants of the nickel phthalate ($\mu \rightarrow 0$)

t (°C)	k_f (M^{-1} sec^{-1})	k_d (sec^{-1})	K (M^{-1})
10	1.2×10^5	0.7×10^3	1.8×10^2
15	2.2×10^5	1.1×10^3	2.0×10^2
20	3.7×10^5	1.7×10^3	2.2×10^2
25	6.3×10^5	2.6×10^3	2.4×10^2
30	10.4×10^5	4.0×10^3	2.6×10^2

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[10] S. Harada, K. Amidaiji, and T. Yasunaga, *ibid.*, **45**, 1752 (1972).

[11] M. Yasuda, K. Yamasaki, and H. Ohtaki, *ibid.*, **33**, 1067 (1960).

[12] J. Kielland, *J. Amer. Chem. Soc.*, **59**, 1675 (1937).

k_f and k_d should coincide with the first estimated K value. The above procedures were repeated until a constant K value was obtained. The final results at each temperature are shown in Fig. 2. The values of the ionic concentrations, the ionic strengths, and the mean activity coefficients in Table 1 are referred to the final result at 25 °C. The rates and the stability constants obtained at various temperatures are given in Table 2.

The Arrhenius energies of activation, $\Delta E_f^{\neq}$ and $\Delta E_d^{\neq}$, were obtained from the plot of log k_f and log k_d respectively against $1/T$. Other thermodynamic parameters of the complex formation. *i.e.*, the entropy of activation, $\Delta S_f^{\neq}$, the enthalpy of activation, $\Delta H_f^{\neq}$, and the free energy of activation, $\Delta G_f^{\neq}$, were calculated from the following equations; they are listed in Table 3:

$$\log A = \log\frac{eRT}{Nh} + \frac{\Delta S_f^{\neq}}{2.3R} \tag{3}$$

$$\Delta H_f^{\neq} = \Delta E_f^{\neq} - RT \tag{4}$$

$$\Delta G_f^{\neq} = \Delta H_f^{\neq} - T\Delta S_f^{\neq} \tag{5}$$

where A is the frequency factor.

Discussion

The stability constants in Table 4 show that the oxalate, malonate, and malate ligands make very stable five- or six-membered chelate complexes, coordinating their carboxyl group or hydroxyl group to the nickel ion. Meanwhile, the succinate, adipate, maleate, and phthalate ligands make much less stable complexes. A definite difference can also be seen in the complex dissociation rate constant. Since the complexes in the former group are stable as chelates, the characteristics of the ligands, *e.g.*, the carbon number and the substituted groups, may be reflected very much in the stabilities and the dissociation rate constants of the complexes. In the latter group, on the other hand, the dissociation rate constants nearly all have the same value, $(2\sim4)\times10^3$ sec^{-1}, and the differences between the ligands are very small compared to the case of the former group. Moreover, the values are very close to the complex dissociation rate constants, k_d' reported by Hoffmann *et al.*:[5-7]

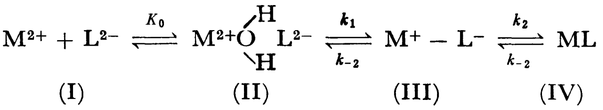
TABLE 3. KINETIC DATA OF THE NICKEL PHTHALATE COMPLEX FORMATION AT 25 °C ($\mu \to 0$)

K, M^{-1}	2.4×10^2
k_f, M^{-1} sec^{-1}	6.3×10^5
k_d, sec^{-1}	2.6×10^3
$E_f^{\neq}$, kcal mol^{-1}	18
$E_d^{\neq}$, kcal mol^{-1}	15
$\Delta G_f^{\neq}$, kcal mol^{-1}	11
$\Delta H_f^{\neq}$, kcal mol^{-1}	18
$\Delta S_f^{\neq}$, cal deg^{-1} mol^{-1}	27
K_0, M^{-1}	25
k_1, sec^{-1}	2.5×10^4

$$\mathrm{Ni(H_2O)_5L} \xrightarrow{k_d'} \mathrm{Ni(H_2O)_6^{2+}} + \mathrm{L^{2-}}. \tag{6}$$

These facts imply that the complex is plausible as a monodentated form rather than as a chelate.

The generally accepted mechanism for the complex-formation reactions is a step-by-step mechanism proposed by Eigen *et al.*[2] The scheme may be represented as follows:



$$\underset{(\mathrm{I})}{\mathrm{M^{2+} + L^{2-}}} \overset{K_0}{\rightleftharpoons} \underset{(\mathrm{II})}{\mathrm{M^{2+}O\genfrac{}{}{0pt}{}{H}{H}\ L^{2-}}} \underset{k_{-2}}{\overset{k_1}{\rightleftharpoons}} \underset{(\mathrm{III})}{\mathrm{M^+ - L^-}} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \underset{(\mathrm{IV})}{\mathrm{ML}} \tag{7}$$

where (I) is the free ion, (II) is the outer-sphere complex, (III) is the monodentated complex, (IV) is the bidentated chelate complex, and K_0 is the outer-sphere complex formation constant. If the complex is considered to be very stable as a chelate, the overall rate constants are related to the rate constants of each step in Reaction (7) as follows:

$$k_f = K_0 k_1\left(\frac{k_2}{k_2 + k_{-1}}\right) \tag{8}$$

TABLE 4. RATES AND STABILITY CONSTANTS OF THE NICKEL DICARBOXYLATE COMPLEXES AT 25 °C

Ligand	k_f (M^{-1} sec^{-1})	k_d (sec^{-1})	K (M^{-1})	μ	Reference
Oxalate	7.4×10^4	3.6	2.1×10^4	0.1	3
	5.2×10^5	3.6	1.4×10^5	—	7
	—	—	2.0×10^5	0.1	1
Malonate	7.0×10^4	44	1.6×10^3	0.1	4
	4.2×10^5	35	1.2×10^4	→0	15[a]
	—	—	1.6×10^3	0.1	11
Succinate	5.8×10^5	4×10^3	2.1×10^2	→0	15[a]
	—	—	40	0.1	11
Adipate	8.5×10^5	4×10^3	2.1×10^2	—	7
	—	—	40	0.1	11
Maleate	8.4×10^5	2.1×10^3	4×10^2	→0	9
	—	—	1.0×10^2	0.1	11
Phthalate	6.3×10^5	2.6×10^3	2.4×10^2	→0	This work
Malate	5.6×10^5	17	3×10^4	→0	10

a) The reported rate constants at 20 °C were converted to the value at 25 °C.

$$k_d = k_{-1}\left(\frac{k_{-2}}{k_2+k_{-1}}\right) \tag{9}$$

If a further assumption is made that the first bond formation between the nickel ion and the phthalate ligand is the rate-determining step, Eq. (9) becomes:

$$k_d = k_{-1}\cdot\frac{k_{-2}}{k_2}. \tag{10}$$

This equation shows that if the complex is a stable chelate, *i.e.*, $k_{-2}/k_2 \ll 1$, k_{-1} will be much larger than $10^4\,\text{sec}^{-1}$. This is implausible as a value of k_{-1}. On the other hand, Hoffmann *et al.*[5-8] determined all of the rate constants in Reaction (7) on the assumptions that K_0k_1 is the same for all the nickel dicarboxylates and is equal to the k_d of the adipate, and that k_{-1} can be assumed from the linear correlation between k_{-1} and the basicity of the carboxylate group. If we try to apply the same procedures to the nickel phthalate system, the rate constants will be given as follows: $K_0k_1=8.5\times10^5\,\text{M}^{-1}\,\text{sec}^{-1}$, $k_{-1}=4\times10^3\,\text{sec}^{-1}$, $k_2=1.1\times10^4\,\text{sec}^{-1}$, and $k_{-2}=1.0\times10^4\,\text{sec}^{-1}$ at 25 °C. The result that k_2 is nearly equal to k_{-2}, however, means that the monodentated complex and the chelate complex are present in comparable concentrations; hence, it is in conflict with the above assumption that the chelate complex is very stable.

The stability constant, K, is given by this equation:

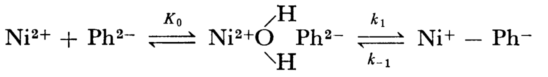
$$K = K_0 + K_0K_1 + K_0K_1K_2 \tag{11}$$

where K_0 can be calculated by the Fuoss equation[13] to be $25\,\text{M}^{-1}$ at $\mu=0$, and where $K_1=k_1/k_{-1}$ and $K_2=k_2/k_{-2}$. On the assumptions that k_1 is equal to the water-exchange rate constant on the nickel ion,[14] $2.7\times10^4\,\text{sec}^{-1}$, and that k_{-1} is found to be $4\times10^3\,\text{sec}^{-1}$ from the Hoffmann relationship between k_{-1} and the basicity of the ligand, K_1 can be calculated to be about 7. Therefore, Eq. (11) can be rewritten as:

$$K = 25(1+7+7K_2) \tag{12}$$

If the complex is stable as a chelate, *i.e.*, $K_2\gg1$; then, K will become much larger than $2\times10^2\,\text{M}^{-1}$. In the nickel phthalate system, however, the stability constant obtained is $2.4\times10^2\,\text{M}^{-1}$; this means that $K_2<1$, *i.e.*, that the monodentated complex is more stable than the chelate complex. In most of the previous studies of the nickel dicarboxylate complex-formation reactions, the concentration of the monodentated complex has been assumed to be negligibly small in comparison with those of the free ions and the chelate complex, but this assumption can not be properly applied to the nickel phthalate system, just as in the nickel maleate system.[8)]

If we assume that the concentration of the chelate complex is negligibly small in comparison with that of the monodentated species, Reaction (7) can be simplified to the following mechanism:



$$\mathrm{Ni^{2+} + Ph^{2-}} \underset{}{\overset{K_0}{\rightleftharpoons}} \mathrm{Ni^{2+}O\begin{smallmatrix}H\\H\end{smallmatrix}\,Ph^{2-}} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Ni^{+} - Ph^{-}} \tag{13}$$

(I) (II) (II)

where $\mathrm{Ph^{2-}}$ means the phthalate ion. Taking into account the facts that the formation and the dissociation of the outer-sphere complex are very fast and that $K_0\gamma_\pm^2(C_{\mathrm{Ni}}+C_{\mathrm{Ph}})$ is much smaller than unity, the relaxation time of the rate-determining step of Reaction (13) is given by the equation:

$$1/\tau = K_0k_1\gamma_\pm^2(C_{\mathrm{Ni}}+C_{\mathrm{Ph}}) + k_{-1}. \tag{14}$$

Since the concentration of the outer-sphere complex is small, the overall stability constant is given as follows:

$$K = K_0\cdot\frac{k_1}{k_{-1}} = \frac{k_f}{k_d} \tag{15}$$

By comparing Eq. (14) with Eq. (2), the following equations were obtained:

$$k_f = K_0k_1 \tag{16}$$

$$k_d = k_{-1} \tag{17}$$

With the values of k_f and K_0, k_1 was calculated to be $2.5\times10^4\,\text{sec}^{-1}$; this value is very close to the water-exchange rate constant on the nickel ion. Moreover, k_{-1}, which is equal to k_d, is equal to the value estimated from Hoffmann's rule and the basicity of the ligand. These good coincidences of the rate constants suggest that the above discussion is correct and that the complex is stable as a monodentated form rather than as a chelate in the case of the nickel phthalate. The rate-determining step of the complex formation is the loss of the water molecule from the inner-sphere of the nickel ion when the monodentated complex is formed.

In addition to the nickel phthalate, pressure-jump studies were also carried out on the nickel complexes of the isophthalate and the terephthalate ligands; however, no relaxation effect was observed in these solutions. This is the same tendency as that observed in the maleate complex and the fumarate complex, where the relaxation effect was observed only in the former solution. From these facts, it may be concluded that the second carboxyl group is not coordinated directly to the nickel ion, but is indispensable in stabilizing the monodentated complex in the nickel complexes of the phthalate and the maleate ligands.

One of the purposes of the present studies has been to ascertain the ligand effect of the seven-membered nickel dicarboxylate complexes. The results obtained above show no systematic relationship between the natures of the ligands and the kinetic values. This may be ascribed to the characteristics of the monodentated form of these complexes.

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