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

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The nickel lactate complex formation reaction in an aqueous solution was studied by the pressure-jump method and the overall rate constants, the stability constants, and the activation parameters were determined. The results were interpreted by the use of the step-by-step complex formation mechanism, and it was revealed that the rate-determining step is the chelate-ring formation process. The ligand effect on the rate of the complex formation was also considered.

With the help of the relaxation techniques,[1,2] fast metal complex formation reactions in solution have been studied. In many cases, the relaxation effects have been interpreted by the step-by-step mechanism,[3] and it has been revealed that the rate-determining step is the dissociation of a water molecule from the inner-coordination sphere of the metal ion. For the complex formation with the bidentate ligand, one more step of chelation should be added to the unidentate-complex-formation mechanism. Kinetic studies of some of the nickel dicarboxylate-complex-formation reactions have been performed[4–7] by the use of the above mechanism. For the assignment of the relaxation effect, however, two different theories have been proposed. In one theory,[4,5] the rate-determining step was considered to be the first-bond formation between the nickel ion and the ligand. In the other,[6,7] it was ascribed to the chelation process. The present authors have studied the nickel dicarboxylate-complex-formation reactions[8–10] and discussed if one of the two theories can be properly applied. In the present studies, the same attempts have also been made in the case of the univalent-bidentate-ligand complex of the nickel ion. The results obtained will be compared to the kinetic data of other bidentate-ligand complexes.

Experimental

All of the chemicals used were of a reagent grade. A stock solution of the nickel lactate was prepared by mixing a stoichiometric amount of $NiSO_4$ and lactic acid where the sulfate ion was precipitated out as $BaSO_4$ by $Ba(OH)_2$ titration. The concentration of the nickel lactate was determined by dimethylglyoxime titration. The solutions studied were prepared by the dilution of the stock solution to the desired concentration. The pH's of the solutions were 5.5—5.8, where most of the ligand was in the dissociated form.

The pressure-jump apparatus used has been described in considerable detail elsewhere.[8] To ensure that the observed relaxation is due to the complex formation reaction of the nickel lactate, blank experiments were carried out with solutions containing only nickel nitrate or sodium lactate under the same conditions. In no case was a relaxation effect observed. The measurements were carried out at 10, 15, 20, 25 and 30 °C in the concentration range from 1.01×10^{-3} to 5.04×10^{-2} M of nickel lactate. The relaxation times quoted are the mean values of at least four runs.

Results and Discussion

The experimental conditions and the reciprocal relaxation times observed at 25 °C are shown in Table 1. The concentration dependence of the relaxation time can be interpreted in terms of the following simple mechanism:

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

where M^{2+} is the metal ion, L^- is the ligand ion, ML^+ is the complex, and k_f and k_d are the formation and the dissociation rate constants respectively. Taking into account the small stability constant and the experimental conditions of the low concentration of the nickel lactate, the concentrations of ML_2 or higher-order complexes are assumed to be negligible. For the mechanism (1), the relaxation time, τ, is related to the rate constants as follows:

$$1/\tau = k_f\gamma_M\gamma_L(C_M+C_L) + k_d\gamma_{ML} \tag{2}$$

where γ is the activity coefficient, C is the equilibrium concentration, and the subscript indicates the corresponding ionic species. Assuming that $\gamma_{ML}=\gamma_L$, Eq. (2) is rearranged to:

$$1/(\tau\cdot\gamma_{ML}) = k_f\gamma_M(C_M+C_L) + k_d. \tag{3}$$

When the stability constant is given, the concentrations of each ionic species can be calculated. The activity coefficients are calculated by the following Davies[11] equation.

$$\log \gamma_i = -\left(\frac{1}{2}\right)\cdot Z_i^2\left(\frac{\mu^{1/2}}{1+\mu^{1/2}} - 0.3\,\mu\right) \tag{4}$$

where Z_i is the charge of the i-th ion and where μ is the ionic strength of the solution. If the suggested

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TABLE 1. RELAXATION TIMES AND EXPERIMENTAL CONDITIONS FOR THE NICKEL LACTATE SYSTEM AT 25 °C

C_0[a] (10^{-4} M)	C_{Ni} (10^{-4} M)	C_L (10^{-4} M)	C_{NiL} (10^{-4} M)	μ (10^{-4})	γ_{Ni}	$\gamma_L = \gamma_{NiL}$	$1/\tau$ (10^2 s^{-1})
10.1	7.9	18.0	2.1	26	0.80	0.95	2.1
20.2	13.4	33.6	6.8	47	0.75	0.93	2.4
40.3	21.0	61.3	19.3	82	0.69	0.91	3.1
60.5	26.3	86.7	34.2	113	0.65	0.90	3.4
100.8	33.6	134.4	67.3	168	0.60	0.88	4.1
201.6	43.2	244.8	158.5	288	0.53	0.85	5.0
302.4	48.3	350.7	254.1	399	0.49	0.84	5.4
403.2	51.6	454.8	351.7	506	0.46	0.82	6.7
504.0	53.8	557.8	450.2	612	0.44	0.81	7.1

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

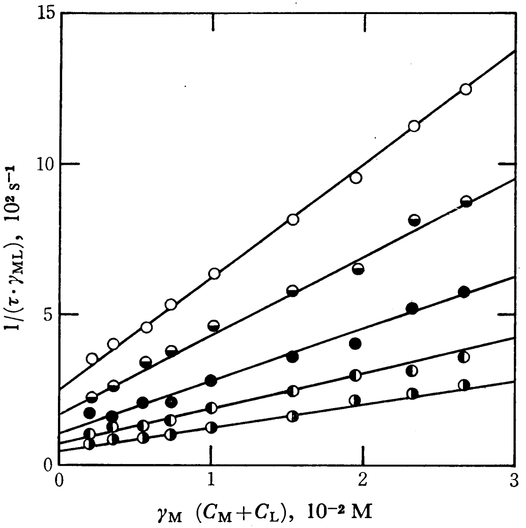

Fig. 1. $1/(\tau \cdot \gamma_{ML})$ *vs.* $\gamma_M(C_M+C_L)$ plot at 10 °C (◑), 15 °C (◐), 20 °C (●), 25 °C (◒), and 30 °C (○).

mechanism is correct, the plot of $1/(\tau \cdot \gamma_{ML})$ *vs.* $\gamma_M(C_M+C_L)$ should be linear; then, k_f and k_d are obtained from the slope and the intercept of the straight line respectively. The stability constant $K(=k_f/k_d)$, which should coincide with the first assumed value, was obtained from the ratio between k_f and k_d. Successive approximations were performed until a constant K was obtained. The final plots at various temperatures are shown in Fig. 1. The lines are the best fit ones based on a least-squares treatment. The rate and the stability constants are summarized in Table 2.

TABLE 2. THE FORMATION AND THE DISSOCIATION RATE CONSTANTS AND THE STABILITY CONSTANTS OF THE NICKEL LACTATE ($\mu \rightarrow 0$)

t, °C	k_f (10^3 M^{-1} s^{-1})	k_d (s^{-1})	K (10^2 M^{-1})
10	7.7±1.0	48±8	1.6±0.4
15	11.5±1.2	72±10	1.6±0.4
20	17.3±1.3	108±22	1.6±0.4
25	26.0±3.1	170±38	1.5±0.4
30	37.5±4.9	250±44	1.5±0.4

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

K, M^{-1}	$1.5(\pm 0.4) \times 10^2$
k_f, M^{-1}s^{-1}	$2.60(\pm 0.31) \times 10^4$
k_d, s^{-1}	$1.70(\pm 0.38) \times 10^2$
$\Delta E_f^{\ddagger}$, kcal·mol^{-1}	13.5±2.3
$\Delta E_d^{\ddagger}$, kcal·mol^{-1}	14.1±3.0
$\Delta G_f^{\ddagger}$, kcal·mol^{-1}	11.4±2.3
$\Delta H_f^{\ddagger}$, kcal·mol^{-1}	12.9±2.3
$\Delta S_f^{\ddagger}$, cal·K^{-1}·mol^{-1}	5±8

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

$$\log A = \log \frac{eRT}{Nh} + \frac{\Delta S_f^{\ddagger}}{2.3R} \qquad (5)$$

$$\Delta H_f^{\ddagger} = \Delta E_f^{\ddagger} - RT \qquad (6)$$

$$\Delta G_f^{\ddagger} = \Delta H_f^{\ddagger} - T\Delta S_f^{\ddagger} \qquad (7)$$

where A is the frequency factor.

The kinetic data obtained for the nickel lactate are compared with the other literature values. The stability constant is very close to the value obtained by Evans *et al.*[12] by the use of conductivity method. The value is also close to the stability constant of the nickel glycollate.[13] At the same time, k_f and k_d are also very close to those of the nickel glycollate.[14] Considering the structural resembrance of the two ligands, the above coincidences of the data can be easily understood. The activation parameters are very close to those of the oxalate[4] and the malonate complexes[5]: *i.e.*, $\Delta E_f^{\ddagger}$=14—16 kcal·mol^{-1}, $\Delta H_f^{\ddagger}$=13—15 kcal·mol^{-1}, $\Delta S_f^{\ddagger}$=5—16 cal·mol^{-1}·K^{-1}, and $\Delta G_f^{\ddagger}$= 10—11 kcal·mol^{-1}. These coincidences imply that the relaxations observed result from similar reactions.

The lactate ligand makes a chelate complex where the carboxyl group and the hydroxyl group are coordinated to the nickel ion. Therefore, the complex

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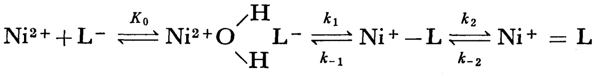
TABLE 4. THE RATE AND THE STABILITY CONSTANTS FOR THE NICKEL CARBOXYLATE COMPLEXES AT 25°C

Ligard	K (M^{-1})	k_f ($M^{-1}s^{-1}$)	k_d (s^{-1})	K_0k_1 ($M^{-1}s^{-1}$)	k_{-1} (s^{-1})	k_2 (s^{-1})	k_{-2} (s^{-1})	Ref.
Oxalate	2.1×10^4	7.4×10^4	3.6	8.5×10^5	7×10^3	6.7×10^2	4	4[a]
Glycollate	1.65×10^2	3.3×10^4	2×10^2	1.5×10^5	9×10^3	2.5×10^3	2.6×10^2	14
Lactate	1.5×10^2	2.6×10^4	1.7×10^2	1.5×10^5	9×10^3	1.9×10^3	2.1×10^2	This work

a) The rate constant of the individual steps were calculated from the original data in the same way as that carried out in the nickel lactate system.

formation reaction (1) must be composed of the following step-by-step mechanism:



$$\mathrm{Ni}^{2+}+\mathrm{L}^- \overset{K_0}{\rightleftharpoons} \mathrm{Ni}^{2+}\mathrm{O}{<}^{\mathrm{H}}_{\mathrm{H}}\ \mathrm{L}^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Ni}^+-\mathrm{L} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{Ni}^+=\mathrm{L} \quad (8)$$

(I) (II) (III) (IV)

where (I) is the free ions, (II) is the outer-sphere complex, (III) is the unidentated complex (probably coordinated by the carboxyl group), (IV) is the chelate complex, and K_0 is the outer-sphere stability constant. The observed relaxation phenomena can be characterized by a single relaxation time; therefore, it may be ascribed to one of the steps in the above mechanism. On the assumption that the intermediate species, (II) and (III), are in the steady state, the rate constants in Eq. (8) are related to the overall formation and the dissociation rate constants, k_f and k_d, in Eq. (1) by the following equations:

$$k_f = K_0k_1\left(\frac{k_2}{k_2+k_{-1}}\right) \quad (9)$$

$$k_d = k_{-1}\left(\frac{k_{-2}}{k_2+k_{-1}}\right). \quad (10)$$

It has usually been admitted[1,3] that k_1 is equal to the water-substitution rate constant of the nickel ion,[15] $2.7\times10^4\,s^{-1}$. Moreover, K_0 can be calculated to be 5.4 M^{-1} for the 2—1 electrolyte by means of this equation:[16,17]

$$K_0 = (4\pi Na^3/3000)\cdot e^{-U(a)/kT} \quad (11)$$

where N is Avogadro's number, $U(a)$ is the Coulomb energy, and a is the distance of the closest approach of ion-pair partners, which was assumed to be 5 Å. Therefore, $K_0k_1=1.5\times10^5\,M^{-1}\,s^{-1}$. The same value of K_0k_1 is also obtained from the kinetic studies of the nickel acetate. The fact that k_f in Table 2 is about an order of magnitude smaller than K_0k_1 means that the value in the parentheses in Eq. (9) is much smaller than unity, *i.e.*, $k_2 \ll k_{-1}$, and that the rate-determining step of the complex formation is not the first-bond formation, but the chelate-ring formation step. If the value of k_{-1} is given, k_2 and k_{-2} can be calculated from Eqs. (9) and (10) by the use of k_f and k_d. Hoffmann *et al.*[7,14] have reported that log k_{-1} bears a linear relationship to the basicity of the ligand. Applying this relationship to the lactate complex, k_{-1} was estimated to be $9\times10^3\,s^{-1}$. By the use of these values, k_2 and k_{-2} were calculated; they are listed in Table 4. The data in Table 4 show that the rate-determining step of the complex formation is the chelation step of the OH group and that of the complex dissociation process is the chelate-ring rupture.

The rate constants of all the steps of the lactate complex formation are very close to those of the glycollate. This means that the rate constants and the stability constants are not affected by the small difference in structure between the two ligands. In comparison with the six-membered dicarboxylate complex, *i.e.*, the oxalate, the lactate is two orders less stable; this may be ascribed not only to the stabilities of the ion-pair formation, but also, and mainly, to the stabilities of the chelate or the rate of the chelate-ring rupture.

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