BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 47 (3), 769—770 (1974)

Kinetic Studies of the Nickel Glycolate Complex Formation in Solution by the Pressure-Jump Method

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(Received December 17, 1973)

Synopsis. The nickel glycolate complex formation reaction was studied by the pressure-jump method and the kinetic parameters were obtained. The rate-determining step of the reaction was revealed to be the chelate-ring formation process.

Glycolate ion makes a chelate complex with a metal ion where COO^- group and OH group are coordinated. The step-by-step model will be, then, proposed for the complex formation mechanism.[1,2] In the previous studies on the kinetics of the nickel lactate complex formation,[3] the authors showed that the rate-determining step is the chelate-ring closure and compared the results with those of the nickel glycolate. On the nickel glycolate complex formation reaction, a few kinetic data have been provided[4-6] but the detailed interpretations have not been reported. By obtaining the kinetic data on the nickel glycolate in the same procedures as that applied to the nickel lactate,[3] the authors aimed to study the ligand effects on the complex formation reaction.

Experimental

All of the chemicals used were of a reagent grade. Sample solutions were prepared in the same way as that described in the previous papers.[3,7] Kinetic studies were carried out by the pressure-jump method which has been described elsewhere.[3,7] 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 the nickel glycolate. Experiments were carried out at least five times for each solution and the quoted relaxation times were the mean values.

Results and Discussion

The concentration dependency of the relaxation times showed that the relaxation phenomena can be interpreted in terms of the following 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, k_f and k_d are the formation and the dissociation rate constants respectively. In Eq. (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 of the species, and the subscripts indicate the corresponding species. Assuming that $\gamma_{ML}=\gamma_L$, Eq. (2) is converted to:

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

If the stability constant, $K(=k_f/k_d)$, is given appropriately, the plot of $1/(\tau\cdot\gamma_{ML})$ *vs.* $\gamma_M(C_M+C_L)$ will be linear; then k_f and k_d can be obtained from the slope and the intercept of the straight line respectively. Here, the activity coefficients were calculated by the Davies equation.[8] Most probable plots at each temperatures are shown in Fig. 1. The rates and the stability constants obtained are summarized in Table 1. Activation parameters were calculated in the same way as that described in the previous papers.[3] They are listed in Table 2. Taking into account the differences of the experimental conditions and the method, the

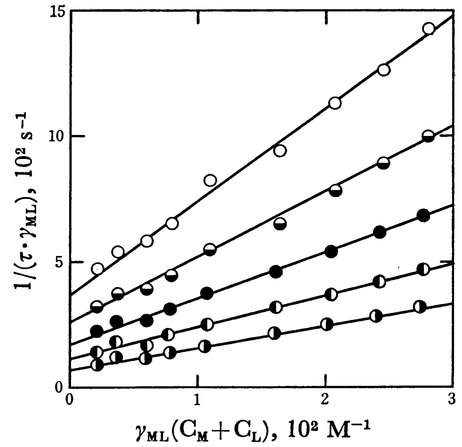


Fig. 1. $1/(\tau\cdot\gamma_{ML})$ *vs.* $\gamma_M(C_M+C_L)$ plot at 10 °C (◑), 15 °C (◐), 20 °C (●), 25 °C (◒), and 30 °C (○).

TABLE 1. THE FORMATION AND THE DISSOCIATION RATE CONSTANTS AND THE STABILITY CONSTANTS OF THE NICKEL GLYCOLATE ($\mu\rightarrow0$)

t, °C	k_f (10^3M^{-1}s^{-1})	k_d (s^{-1})	K (10^2M^{-1})
10	8.7±0.6	72±5	1.2±0.1
15	12.5±0.6	114±5	1.1±0.1
20	18.7±0.6	170±10	1.1±0.1
25	26.0±1.0	260±15	1.0±0.1
30	37.0±1.5	370±20	1.0±0.1

TABLE 2. KINETIC DATA OF THE NICKEL GLYCOLATE COMPLEX FORMATION AT 25 °C ($\mu\rightarrow0$)

K, M^{-1}	$1.0(\pm0.1)\times10^2$
k_f, M^{-1}s^{-1}	$2.60(\pm0.10)\times10^4$
k_d, s^{-1}	$2.60(\pm0.15)\times10^2$
$\Delta E_f^{\neq}$, kcal·mol^{-1}	12.5±1.1
$\Delta E_d^{\neq}$, kcal·mol^{-1}	13.8±1.0
$\Delta G_f^{\neq}$, kcal·mol^{-1}	11.4±1.1
$\Delta H_f^{\neq}$, kcal·mol^{-1}	11.9±1.1
$\Delta S_f^{\neq}$, cal·deg^{-1}·mol^{-1}	2±4

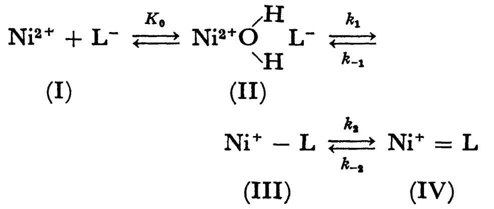
Table 3. The rate and the stability constants for the nickel carboxylate complexes at 25 °C

Ligand	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})	ΔE_f^{*} ($kcal\cdot mol^{-1}$)	μ	Ref.
Oxalate	2.1×10^4	7.4×10^4	3.6	8.5×10^5	7×10^3	6.7×10^2	4	15	0.1	2[a]
Malonate	1.0×10^4	4.5×10^5	45	8.5×10^5	3.5×10^3	4.5×10^3	1×10^2	—	—	5
	1.2×10^4	4.2×10^5	35	8.5×10^5	3.5×10^3	3.4×10^3	70	14.2	→0	12[a]
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	13.5	→0	3
Glycolate	1.0×10^2	2.6×10^4	2.6×10^2	1.5×10^5	9×10^3	1.9×10^3	3.2×10^2	12.5	→0	This work
	1.7×10^2	3.3×10^4	2.0×10^2	1.5×10^5	9×10^3	2.5×10^3	2.6×10^2	—	—	6

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

stability constants in Table 2 are in good agreement with the literature values.[9–11] The rate constants at 25 °C are in fair agreement with the data of the nickel glycolate reported by Hoffmann.[6] The activation parameters are close, not only, to those of the lactate but also to the oxalate and the malonate.[12] These resembrances imply that the same step of the reaction, *e.g.*, chelate-ring closure, is responsible for the present relaxation phenomena.

The detailed model of the nickel glycolate complex formation can be expressed as follows:



$$\underset{\text{(I)}}{\mathrm{Ni^{2+} + L^-}} \overset{K_0}{\rightleftarrows} \underset{\text{(II)}}{\mathrm{Ni^{2+}O{<}^{H}_{H}\ L^-}} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \underset{\text{(III)}}{\mathrm{Ni^+ - L}} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \underset{\text{(IV)}}{\mathrm{Ni^+ = L}} \qquad (4)$$

where (I) is the free ions, (II) is the outer-sphere complex, (III) is the unidentated complex, (IV) is the chelate complex, and K_0 is the outer-sphere complex formation constant.

Assuming that the complex is stable as a chelate complex and the intermediate state (II) and (III) are in the steady state, the rate constants in Eq. (4) are related to k_f and k_d in Eq. (1) as follows:

$$k_f = K_0k_1\left(\frac{k_2}{k_2+k_{-1}}\right) \qquad (5)$$

$$k_d = k_{-1}\left(\frac{k_{-2}}{k_2+k_{-1}}\right) \qquad (6)$$

As that described in the previous paper,[3] K_0k_1 and k_{-1} can be estimated to be $1.5\times10^5\,M^{-1}\,s^{-1}$ and $9\times10^3\,s^{-1}$, respectively. Then, k_2 and k_{-2} can be obtained by Eqs. (5) and (6). They are listed in Table 3 along with the rate constants of the other nickel bidentate complexes.

In the nickel glycolate complex formation, the rate-determining-step is the chelate-ring closure step. The kinetic data are very close to those of the nickel lactate. This fact shows that the methyl group of the lactate ion does not give effective contributions to the kinetic values of the complex formation. In Table 3, the rate constants of the chelate-ring closure, k_2, are of the order of $\sim10^3\,s^{-1}$, which is about an order of magnitude smaller than the water exchange rate constant of the nickel ion. This fact means that the values of the rate constants of the chelate-ring rupture, k_{-2}, reflect the stabilities of the chelate complexes.

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