1752 BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 1752—1755 (1972) [Vol. 45, No. 6

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

Shoji Harada, Katsuyoshi Amidaiji, and Tatsuya Yasunaga
Department of Chemistry, Faculty of Science, Hiroshima University, Higashisenda-machi, Hiroshima

(Received December 21, 1971)

The nickel malate complex formation reaction in an aqueous solution, $Ni^{2+}+Mal^{2-} \underset{k_d}{\overset{k_f}{\rightleftharpoons}} NiMal$, where Mal^{2-} represents the malate ion, was studied by the pressure-jump method. The following rate constants and the equilibrium constant were obtained: $k_f=5.6\times10^5\ \text{M}^{-1}\ \text{sec}^{-1}$, $k_d=17\ \text{sec}^{-1}$ and $K=3\times10^4\ \text{M}^{-1}$ at 25°C and $\mu\rightarrow0$. Studies at various temperatures between 12 and 30.5°C gave the thermodynamic parameters. In comparison with the results on other ligand complexes, the ligand effects seem to be found not in the formation rate constant, but in the dissociation rate constant. The results indicate that the rate-determining step of the complex formation is the release of the water molecule from the inner coordination sphere of the nickel ion.

The development of the relaxation method has made it possible to study kinetically the fast metal complex formation reactions.[1] Some of the complex formations of the nickel(II) ion have been studied by the flow method,[2] the temperature-jump method,[3] the pressure-jump method[4], and most recently by the pressure-shock method.[5] These studies have revealed that the step-by-step association picture proposed by Eigen[6] *et al.* for the complex formation reaction is valid and that the rate-determining step is the release of the water molecule from the inner coordination sphere of the nickel ion. In the case of the complex formation with a bidentate ligand, however, two water molecules on the nickel ion should be replaced, and the reaction mechanism is more complicated.

The present study was undertaken in order to obtain kinetic information on the nickel malate complex formation reaction and in order to compare the ligand effects on the kinetic parameters with those of other bidentate ligands. Another purpose was to test the operation of a newly-built device at the beginning of the pressure-jump study.

Experimental

All of the chemicals used were of a reagent grade. A stock solution of nickel malate was prepared by mixing a stoichiometric amount of $NiSO_4$ with malic acid, and then it was titrated with a solution of $Ba(OH)_2$ until all the sulfate ion had precipitated as $BaSO_4$. The solid $BaSO_4$ was removed by filtration. The concentration of the nickel malate of the resultant solution was determined by a dimethylglyoxime titration. Each solution studied was prepared by diluting the stock solution to the desired concentration. The pH values of the solutions were $\geqq6.5$ where most of the ligand was in the dissociated form. In order to reduce the cavitation effects, the solutions were degassed by sonoration with a 400 KHz transducer under reduced pressure.

The pressure-jump apparatus used was a modification of that described by Macri and Petrucci.[7] The pressure-jump cell is shown in Fig. 1. N_2 gas was introduced from the gas inlet until a brass diaphragm burst at a pressure of approximately 25 atm. The pressure of the two cells, one containing the sample solution and the other containing the reference KCl solution, decreases abruptly from 25 to 1 atm. The concentration changes of the species were followed by means of the electric conductivity method; *i.e.*, the two cells were in separate arms of a Wheatstone bridge circuit fed from a 150 KHz oscillator. To calibrate the time constant of the apparatus, a 0.02 M $MgSO_4$ solution which exhibites a relaxation effect faster than 1 μsec was used. From the trace obtained (Fig. 2a), the apparatus has been proved to be useful for kinetic studies of reactions with relaxation times down to 100 μsec. The temperature of the sample cell was controlled to ±0.5°C by circulating the water from a thermostat through a copper tube spiraled around the cell.

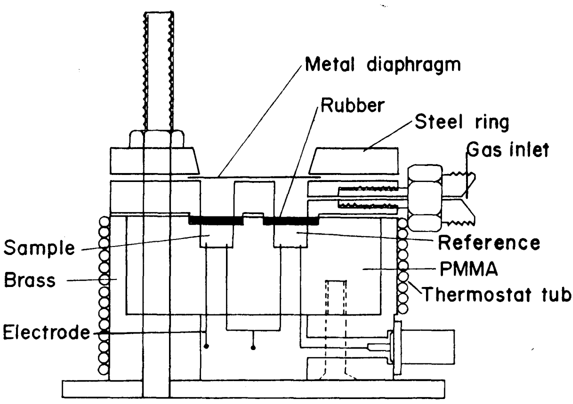

Fig. 1. Pressure-jump cell.

In all the nickel malate solutions, the relaxation spectrum was characterised by a single relaxation time. A representative relaxation spectrum is shown in Fig. 2b. The reciprocal relaxation time was calculated from a plot of $-\log \Delta C$ *vs.* the time, where ΔC is the deviation of the concentration from its equilibrium value. The quoted relaxation times and the rate constants are the mean values of several runs.

---

[1] M. Eigen and L. DeMaeyer, "Technique of Organic Chemistry", Vol. VIII, 2nd Ed., S. L. Friess, Interscience Publishers Inc., New York, N. Y. (1963), Part 2, p. 895.

[2] G. H. Nancollas and N. Sutin, *Inorg. Chem.*, **3**, 360 (1964).

[3] G. G. Hammes and J. I. Steinfeld, *J. Amer. Chem. Soc.*, **84**, 4639 (1962).

[4] J. L. Bear and C. T. Lin, *J. Phys. Chem.*, **72**, 2026 (1968).

[5] H. Hoffmann and E. Yeager, *Ber. Bunsenges. Physik. Chem.*, **74**, 641 (1970).

[6] M. Eigen and K. Tamm, *Z. Elektrochem.*, **66**, 93, 107 (1962).

[7] G. Macri and S. Petrucci, *Inorg. Chem.*, **9**, 1009 (1970).

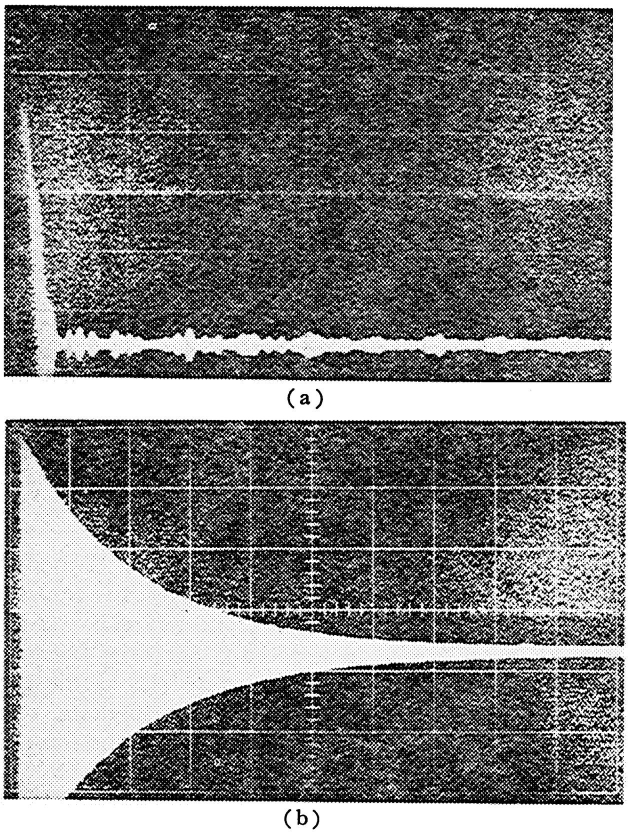

Fig. 2. Pressure-jump spectra.
(a) 0.02 M $MgSO_4$; sweep 200 μsec/division,
(b) 29.2×10^{-4} M Nickel malate; sweep 2 msec/division at 25°C.

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

C_0[a)] (10^{-4} M)	C_{Nimal} (10^{-4} M)	$C_{\mathrm{Ni}}=C_{\mathrm{mal}}$ (10^{-5} M)	μ (10^{-4})	$\gamma_\pm$	$1/\tau$ (sec^{-1})
6.8	5.5	13.0	5.2	0.90	136
9.8	8.2	15.8	6.3	0.90	160
19.5	17.2	22.8	9.1	0.88	206
29.2	26.4	28.2	11.3	0.86	284
39.0	35.7	32.8	13.1	0.85	310
58.5	54.4	40.5	16.2	0.84	348
78.0	73.3	47.0	18.8	0.83	371
117.0	111.2	57.8	23.1	0.82	445
156.0	149.3	67.0	26.8	0.80	510
195.0	187.5	75.0	30.0	0.79	576
234.0	225.8	82.3	32.9	0.79	585
273.0	264.1	89.0	35.6	0.78	626
312.0	302.5	95.3	38.1	0.77	700
351.0	340.9	101.2	40.5	0.77	670
390.0	379.3	106.8	42.7	0.76	635

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

Results

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, and ML is the complex. The rate constants are related to the relaxation time, τ, by the following equation:

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

where C_M and C_L are the concentrations of M^{2+} and L^{2-} respectively and where $\gamma_\pm$ is the mean activity coefficient of the free ions. The experimental conditions and the observed relaxation times at 25°C are shown in Table 1.

The complex formation constant, $K(=k_f/k_d)$, of nickel malate was not, unfortunately, given in the literature, so the values of k_f, k_d, and K were calculated from the kinetic data. As the first approximation, a value of K which had been roughly estimated from those of nickel malonate and succinate[8)] was used to calculate the ionic concentrations. The activity coefficients of the ions were calculated by means of the Kielland equation.[9)] The $1/\tau$ values were plotted against $\gamma_\pm^2(C_M+C_L)$ to give k_f and k_d from the slope and the intercept of the line respectively. Here, the ratio of k_f and k_d should coincide with the first estimated K value. The same procedures were repeated until a constant K value was obtained. The final results are shown in Fig. 3, and the following rate and equilibrium constants were obtained: $k_f=5.6\times10^5\ \mathrm{M}^{-1}\mathrm{sec}^{-1}$, $k_d=17\ \mathrm{sec}^{-1}$, and $K=3\times10^4\ \mathrm{M}^{-1}$ at 25°C $\mu\rightarrow0$.

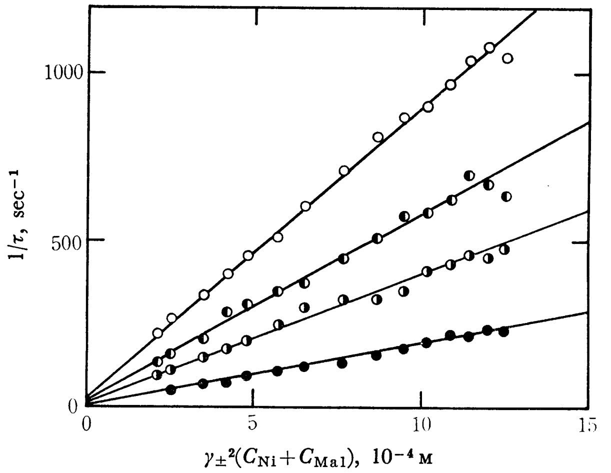

Fig. 3. $1/\tau$ vs. $\gamma_\pm^2(C_{\mathrm{Ni}}+C_{\mathrm{Mal}})$ plot at 12°C (●), 20°C (◑), 25°C (◐), and 30.5°C (○).

In order to determine the energies of activation, a series of experiments was run covering the temperature range from 12 to 30.5°C. The rate constants, k_f, and k_d, and the equilibrium constants at each temperature were obtained from Fig. 3. The Arrhenius energy of activation, $\Delta E_f^{\neq}$, was obtained from the plot of $\log k_f$ against $1/T$, as is shown in Fig. 4. 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 next

---

8) R. M. Fuoss, *J. Amer. Chem. Soc.*, **80**, 5059 (1958).
9) J. Kielland, *ibid.*, **59**, 1675 (1937).

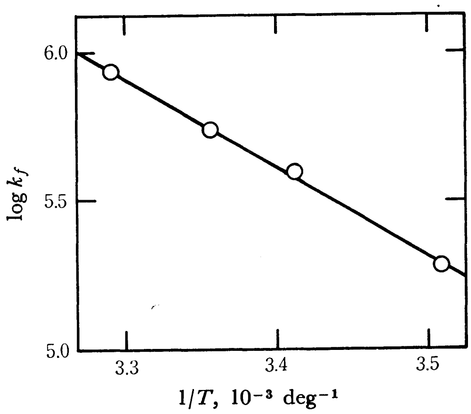

Fig. 4. Temperature dependence of k_f.

Table 2. Kinetic data for the nickel malate complex formation at 25°C ($\mu \to 0$)

$$\mathrm{Ni^{2+} + Mal^{2-}} \underset{k_d}{\overset{k_f}{\rightleftharpoons}} \mathrm{NiMal}$$

K, M^{-1}	3×10^4
k_f, M^{-1} sec^{-1}	5.6×10^5
k_d, sec^{-1}	17
$E_f^{\ddagger}$, kcal mol^{-1}	14
$\Delta G_f^{\ddagger}$, kcal mol^{-1}	10
$\Delta H_f^{\ddagger}$, kcal mol^{-1}	13
$\Delta S_f^{\ddagger}$, cal deg^{-1} mol^{-1}	12
K_0, M^{-1}	25
k_{12}, sec^{-1}	22×10^3
ΔG_0, kcal mol^{-1}	-1.9
ΔH_0, kcal mol^{-1}	3
ΔS_0, cal deg^{-1} mol^{-1}	16
$\Delta H_{12}^{\ddagger}$, kcal mol^{-1}	10
$\Delta S_{12}^{\ddagger}$, cal deg^{-1} mol^{-1}	-4

equations; they are listed in Table 2.

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

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

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

where A is the frequency factor.

Discussion

The kinetic data obtained for the nickel malate systems are compared with those for similar systems in Table 3. The values of k_f lie in approximately the same order, $\sim 10^5$ M^{-1} sec^{-1}, irrespective of the nature of the ligand, and the ligand effects are found not in the value of k_f, but in the values of k_d and K.

Eigen and his co-workeers have proposed[6] a mechanism of complex formation reaction *via* rapid ion-pair formation, followed by the rate-determining loss of a water molecule in the inner coordination sphere of the metal ion:

$$\begin{array}{ccc} \mathrm{Ni(H_2O)_6{}^{2+} + Mal^{2-}} & \overset{K_0}{\rightleftharpoons} & \mathrm{[(H_2O)_5Ni(H_2O)Mal]} \\ \mathrm{I} & & \mathrm{(II)} \end{array}$$
$$\begin{array}{cccc} \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} & \mathrm{[(H_2O)_5NiMal]} & \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} & \mathrm{[(H_2O)_4NiMal]} \\ & \mathrm{(III)} & & \mathrm{(IV)} \end{array} \tag{6}$$

where state (I) is the free ions, state (II) is the ion-pair, state (III) is the half-bonded intermediate, state (IV) is the bidentated complex, and K_0 is the ion-pair association constant.

On the assumptions that the intermediate state (III) is in a steady state and that $k_{23} \gg k_{21}$, the rate constant in Eq. (6) may be thus related to the formation rate constant in Eq. (1):

$$k_f = K_0 \cdot k_{12} \tag{7}$$

K_0 cannot be determined experimentally, so it has become customary to estimate it by means of the Fuoss equation.[3,8] For 2—2 electrolytes, K_0 can be calculated to be about 25 M^{-1}. The rate constant for the rate-determining process of Reaction (6), k_{12}, was, then, calculated to be 2.2×10^4 sec^{-1} by means of Eq. (7).

As may be seen in Table 4, this value has become of interest in comparison with the case of other ligand complexes, *i.e.*, the rate constants of the rate-deter-

Table 3. Rates and complex formation constants of nickel dicarboxylate

Ligand	K, M^{-1}	k_f, M^{-1} sec^{-1}	k_d, sec^{-1}	t, °C	μ	Reference
Oxalate	2.1×10^4	7.5×10^4	3.6	25	0.1	2
Malonate	1.2×10^4	2.7×10^5	24	20	$\to 0$	4
Succinate	2.1×10^2	4.3×10^5	2.7×10^3	20	$\to 0$	4
Malate	3×10^4	5.6×10^5	17	25	$\to 0$	This work

Table 4. Rate constant of the rate-determining process of the nickel complex formation reaction at 25°C

Ligand	k_{12}(10^3 sec^{-1})	Ref.	Ligand	k_{12}(10^3 sec^{-1})	Ref.
Water	27	2	Triglycine	5	10
Imidazole	16	3	Oxalate	6	2
Sulfate[a]	15	6	Malonate[a]	11	4
Glycine	9	3	Succinate[a]	17	4
Diglycine	12	3	Malate	22	This work

a) At 20°C.

---

10) J. I. Steinfeld and G. G. Hammes, *J. Phys. Chem.*, **67**, 528 (1963).

mining process of the nickel complex formation lie approximately 10^3—10^4 $\sec^{-1}$ irrespective of the nature of the entering ligand. The small difference between them may be due to the approximation in calculating K_0. These facts indicate that the loss of a water molecule in the inner coordination sphere of the nickel ion is the rate-determining process of the complex fomration reaction.

Activation parameters can be reevaluated as follows for the detailed mechanism of complex formation in considering the variation in the free energy (ΔG_0), the entoropy (ΔS_0), and the enthalpy (ΔH_0) for the ion-pair formation:

$$\Delta G_0 = -RT \ln K_0 \tag{8}$$

$$\Delta S_0 = -19.4\, Z_- Z_+ / a = \Delta S^{\ne} - \Delta S^{\ne}_{12} \tag{9}$$

$$\Delta H_0 = \Delta G_0 + T\Delta S_0 = \Delta H^{\ne} - \Delta H^{\ne}_{12} \tag{10}$$

where Z is the valence of the ion and where a is the distance of the closest approach of the ion-pair partners (5Å). The results are listed in Table 2. In comparison with the complexes of other ligands, the thermodynamic parameters calculated are of the same order of magnitude, despite the large differences in the nature of the ligands, *e.g.*, the carbon number and the acidity. This fact also suggests that the rate-determining step of the complex formation is the release of the water molecule from the inner-sphere of the nickel ion.

In acid solutions, another path of the nickel malate complex formation can be proposed:

$$\mathrm{Ni^{2+} + HMal^- \rightleftharpoons NiMal + H^+} \tag{11}$$

In this experiment, however, the relaxation effect has become small with an increase in the concentration of $\mathrm{HMal^-}$. Therefore, we could not obtain very precisely the dependency of τ on the hydrogen-ion concentration, as was done in the nickel malonate complex formation reaction.[11]

The authors wish to express their thanks to Mr. Takayasu Goto for the assistance he has given in the construction of the apparatus.

---

[11] F. P. Cavasino, *ibid.*, **69**, 4380 (1965).