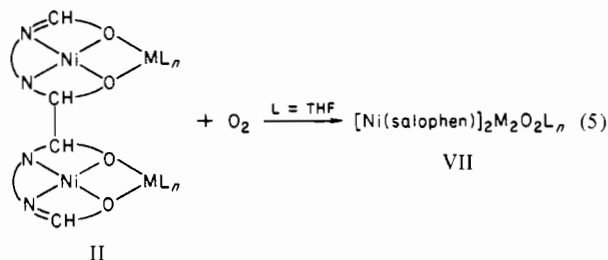


free radical. Hydrogen abstraction from the solvent can explain the formation of methane. Complexes II are able to transfer two electrons to a substrate by a process that cleaves the C-C bond established between the two [Ni(salophen)] units and re-forms two imino groups. The property of II that deserves the main attention is their reducing ability associated with a C-C bond cleavage. Such a C-C bond acts, as a matter of fact, as an electron reservoir. This unique chemical behavior is emphasized by their reaction with O<sub>2</sub>. Complexes II absorb one molecule of O<sub>2</sub>/dimeric unit. The final material (VII) can be recrystallized from DMF giving [Ni(salophen)]. The expected presence of peroxides might be not confirmed by any conventional method (see Experimental Section). The reaction of II with dioxygen is reported in eq 5. Absorption of 1 mol



of O<sub>2</sub>/mol of dimer and, therefore, formation of peroxides are independent of the nature of the alkali cation. Formation of peroxides from the alkali metal itself is, on the contrary, highly dependent on the nature of the metal. The analytical identification of complexes VII is prevented by their lability being the cause of a partial decomposition into their components,

i.e., [Ni(salophen)] and alkali peroxides. This is a quite common evolution of such complexes in coordinating solvents and the reason why the treatment with DMF allowed us to break down adduct VII and to recover [Ni(salophen)]. In spite of the fact that reaction 1 does not produce Ni(I) complexes, reactivity of complexes II, however, is that expected for nickel(I) complexes having delocalized ligands. Results so far obtained seem to rule out any attack at the bridging C-C unit by the oxidizing agent. Although the C-C unit is a crucial site of the structure for the electron-transfer process, it does not become a reactive site. Reducing agents like complexes II having different metal centers and two electrons available seem to be rather promising for reducing CO<sub>2</sub> and CO<sub>2</sub>-like molecules.<sup>20</sup>

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**Registry No.** I, 36433-88-2; II (M = Li)·2THF, 87655-37-6; II (M = Li), 87655-36-5; II (M = Na)·C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>, 87655-39-8; II (M = Na), 87655-38-7; VI (M = Li), 87681-04-7; VI (M = Na), 87655-40-1; {[Ni(salophen)Na]<sub>2</sub>(DHCH)}<sub>n</sub>, 87725-96-0; MeI, 74-88-4; Li, 7439-93-2; Na, 7440-23-5; O<sub>2</sub>, 7782-44-7; iodine, 7553-56-2; methane, 74-82-8.

**Supplementary Material Available:** Hydrogen coordinates for complex II (M = Na) (Table SI), thermal parameters (Tables SII and SIII), equations of least-squares planes (Table SIV), and listings of observed and calculated structure factors (32 pages). Ordering information is given on any current masthead page.

(20) Gambarotta, S.; Floriani, C., unpublished results.

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## Kinetic and Equilibrium Studies of Complex Formation of Nickel(II) with Carboxylate Ligands at High Pressure. 1. Nickel(II) Succinate and Nickel(II) Maleate

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Kinetic and equilibrium measurements were carried out for the complex-formation reaction of nickel(II) succinate and nickel(II) maleate in aqueous solution at pressures up to 1000 kg cm<sup>-2</sup>. From the pressure dependence of the stability constant and the rate constant, the reaction volume,  $\Delta V^\ddagger$ , and the activation volume,  $\Delta V_f^\ddagger$ , for the complex formation were estimated to be as follows:  $\Delta V^\ddagger = 11.1 \pm 0.9 \text{ cm}^3 \text{ mol}^{-1}$  and  $\Delta V_f^\ddagger = 14.1 \pm 0.8 \text{ cm}^3 \text{ mol}^{-1}$  for nickel(II) succinate;  $\Delta V^\ddagger = 14.9 \pm 0.4 \text{ cm}^3 \text{ mol}^{-1}$  and  $\Delta V_f^\ddagger = 13.5 \pm 0.6 \text{ cm}^3 \text{ mol}^{-1}$  for nickel(II) maleate. When the volume change accompanied by the outer-sphere complex formation is taken into account, the activation volumes obtained were close to that found for the water-exchange reaction of the aquonickel(II) ion. This result is consistent with the interpretation that the rate-determining step is a water loss from the inner coordination shell of the nickel(II) ion, as postulated in the Eigen mechanism.

### Introduction

Kinetics of the complex-formation reaction of labile metal ions in aqueous solution have been extensively studied after the development of rapid-reaction techniques. The broad outline of the mechanism of these reactions is well understood in terms of the Eigen mechanism,<sup>1</sup> according to which the rate-determining step is the loss of a water molecule from the inner coordination shell of the metal after the formation of an external ion pair (or outer-sphere complex) between metal and ligand. However, some details still need to be elucidated concerning the details of the mechanism. For example, in the case of chelating ligands, the situation is more complicated due to the presence of a ring-closing step. For nickel(II)

monochelate complexes with malonate or substituted malonate anions, some discrepancies are seen in the literature concerning the assignment of the rate-determining step; some assign it to the first bond formation between the nickel(II) ion and the ligand,<sup>2,3</sup> and others to the chelate-ring closure.<sup>4</sup>

From measurements under variable pressure, one can obtain information about the volume change associated with the reaction under study.<sup>5</sup> Kinetic measurements at high pressure

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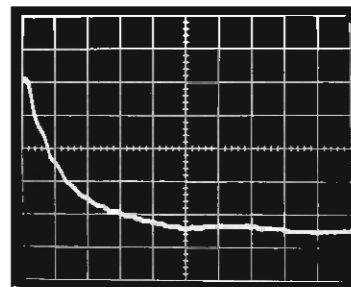
give an activation volume that serves as a useful parameter for the elucidation of the reaction mechanism, and therefore, a number of high-pressure kinetic studies on various systems have been carried out.<sup>6,7</sup> However, most of the studies have been limited to reactions with moderate rates. Recently, rapid-reaction techniques have been improved and applied to high-pressure measurements.<sup>8-13</sup> The application of these techniques to metal complexation reactions<sup>8,13-15</sup> has shown that they are very useful tools for elucidation of the reaction mechanism.

Recently, we have been studying the kinetics and equilibrium of the complex formation between nickel(II) and a variety of carboxylate ligands at high pressure in order to elucidate the reaction mechanism with the aid of information about the volume change. In this paper, the results obtained for the nickel(II) succinate and nickel(II) maleate systems are reported. Kinetic study of the nickel(II) succinate system at atmospheric pressure has been reported by Bear and Lin,<sup>2</sup> where the results have been interpreted in terms of a kinetic model where the chelate-ring closure takes place much faster than the first bond formation and the rate-determining step is the loss of water from the inner coordination shell of the nickel(II) ion. On the other hand, Harada and Yasunaga<sup>16</sup> have suggested on the basis of a detailed analysis of rate constants that nickel(II) succinate and nickel(II) maleate form monodentate complexes, in spite of their molecular structure from which seven-membered chelate complexes are expected. It is of interest to examine whether the volume profile of the reaction may serve as a criterion for the two proposed mechanisms, i.e., monodentate and bidentate.

### Experimental Section

**Materials.** Stock solutions of nickel(II) succinate and nickel(II) maleate were prepared by the following procedure:<sup>2,16</sup> stoichiometric amounts of NiSO<sub>4</sub> and the respective acid were mixed in aqueous solution and then SO<sub>4</sub><sup>2-</sup> was precipitated as BaSO<sub>4</sub> by adding an equivalent amount of Ba(OH)<sub>2</sub> solution. The precipitated BaSO<sub>4</sub> was removed by filtration. The concentrations of nickel(II) succinate and nickel(II) maleate in the stock solutions were determined by EDTA titration. Each sample solution was prepared by diluting the stock solution to the desired concentration. All the reagents were of a guaranteed grade and were used without further purification. The pH of the solution ranged from 6.7 to 6.9 and from 7.2 to 7.5 for nickel(II) succinate and nickel(II) maleate, respectively. In these pH ranges, most of the ligands are in the dissociated form.

**Equilibrium Measurements.** Stability constants of the complexes were determined from the conductivity measurements (the Fuoss-Kraus method<sup>17,18</sup>). A high-pressure apparatus for conductivity measurements was almost the same as described in the literature.<sup>19</sup> Measurements were made by a Yanagimoto conductivity outfit, Model



**Figure 1.** Typical relaxation effect observed in a nickel(II) maleate solution at 10 °C and final pressure of 1000 kg cm<sup>-2</sup>. The concentration of nickel(II) maleate is 1.74 × 10<sup>-3</sup> mol dm<sup>-3</sup>. Time scale is 1 ms/division.

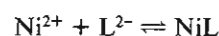
MY-8, at pressures of 1, 200, 400, 600, 800, and 1000 kg cm<sup>-2</sup> and at temperature of 10.0 ± 0.1 °C.

**Kinetic Measurements.** Kinetic measurements for the complexation reaction were carried out by means of pressure-jump (*P*-jump) technique. A high-pressure *P*-jump apparatus with conductivity detection has been described previously.<sup>13</sup> The original signal was interfered with by an artifact that might be introduced by a reflected shock wave from the vessel wall and required about 4 ms to decay. Therefore, the application of the apparatus was limited by the presence of an interference signal only to systems with rather long relaxation times. This interference signal was eliminated considerably by employing the dual-cell system where the effect of the artifact was canceled out by mixing with the signal from the reference cell containing NiSO<sub>4</sub> solution of appropriate concentration. Figure 1 shows a typical relaxation effect obtained with nickel(II) maleate solution. Although a weak interference signal is observed, it is not so strong as to disturb the determination of the relaxation time. The relaxation time,  $\tau$ , was determined by fitting  $Y = A \exp(-t/\tau) + B$  to the time course of the signal shown in Figure 1 by a nonlinear least-squares analysis. Measurements were made at the same pressure and temperature as equilibrium measurements.

### Results

**Equilibrium Study.** Stability constants for nickel(II) succinate and nickel(II) maleate were determined from the conductivity data according to the following procedure. In the present systems, complex formation equilibrium is expressed as in Scheme I, where L<sup>2-</sup> represents the succinate or

#### Scheme I



maleate ion. Then, the thermodynamic stability constant,  $K$ , is given by eq 1 in terms of the analytical concentration,  $c$ ,

$$K = \left( \frac{1 - \alpha}{\alpha^2 c} \right) \left( \frac{\gamma_{\text{NiL}}}{\gamma_{\pm}^2} \right) \quad (1)$$

and the degree of dissociation of the complex,  $\alpha$ , where  $\gamma_{\text{NiL}}$  and  $\gamma_{\pm}$  are the activity coefficient of the complex and the mean activity coefficient of the ions, respectively.  $\alpha$  is related to the equivalent conductivity of the relevant solution,  $\Lambda$ , and that at infinite dilution,  $\Lambda^\circ$ , by<sup>18</sup>

$$\alpha = \Lambda / \Lambda^\circ F \quad (2)$$

where

$$F = \frac{4}{3} \cos^2 \left[ \frac{1}{3} \arccos \left( -\frac{3(3^{1/2})Z}{2} \right) \right] \quad (3)$$

and  $Z$  is defined as

$$Z = (\alpha^* \Lambda^\circ + \beta^*) (\Lambda c)^{1/2} / (\Lambda^\circ)^{3/2} \quad (4)$$

In eq 4,  $\alpha^*$  and  $\beta^*$  are the Onsager parameters whose values are given for a 2-2 electrolyte system by<sup>20</sup>  $\alpha^* = 6.563 \times$

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Table I. Stability Constants,  $K$ ,<sup>a</sup> as a Function of Pressure at 10 °C and  $\mu \rightarrow 0$ 

	$P/\text{kg cm}^{-2}$					
	1	200	400	600	800	1000
nickel(II) succinate	143 (6)	125 (5)	107 (4)	102 (4)	93 (4)	85 (3)
nickel(II) maleate	540 (20)	490 (17)	417 (17)	366 (14)	318 (12)	282 (11)

<sup>a</sup> In  $\text{mol}^{-1} \text{dm}^3$ . Standard deviations derived from the least-squares analysis are shown in parentheses.

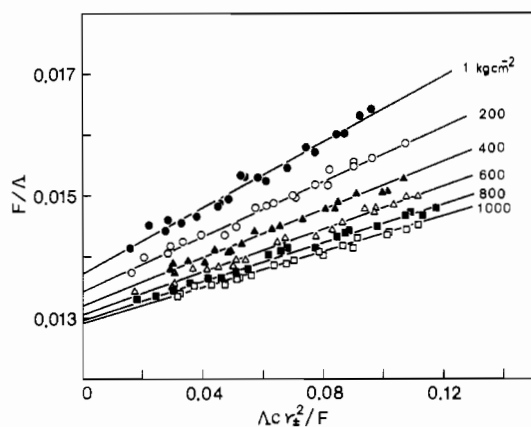


Figure 2. Plot of conductivity data according to eq 5 for nickel(II) succinate at 10 °C. Pressures ( $\text{kg cm}^{-2}$ ) are 1 (●), 200 (○), 400 (▲), 600 (△), 800 (■), and 1000 (□).

$10^6/(\epsilon T)^{3/2}$  and  $\beta^* = 330.0/(\eta(\epsilon T)^{1/2})$ , where  $\epsilon$  is the dielectric constant of the medium,  $\eta$  the solution viscosity, and  $T$  the temperature. Combining eq 1 and 2 and approximating the activity coefficient of the complex in dilute solution to be 1, one obtains

$$\frac{F}{\Lambda} = \frac{1}{\Lambda^\circ} + \left( \frac{K}{(\Lambda^\circ)^2} \right) \left( \frac{\Delta c \gamma_{\pm}^2}{F} \right) \quad (5)$$

From an appropriate initial value of  $\Lambda^\circ$ , a first approximate value of  $F$  is calculated by using eq 3 and 4. Then, an approximate value of  $\alpha$  is estimated from eq 2, from which  $\gamma_{\pm}$  is calculated by the Debye-Hückel equation. These calculated values at several concentrations are plotted according to eq 5, and the intercept of the plot gives a second approximate value of  $\Lambda^\circ$  that is used for the second calculation loop. This procedure is repeated until the constant value of  $\Lambda^\circ$  is obtained, and the value of  $K$  is estimated from the slope and the intercept of the final plot of eq 5.

When the procedure described above is applied to the present systems,  $\Lambda^\circ = 106.0$  (the value for nickel(II) oxalate at 18 °C and atmospheric pressure) was used as an initial value of  $\Lambda^\circ$  and the fitting of eq 5 to the data points was made by a linear least-squares method. The calculation was repeated until  $\Lambda^\circ$  converged to within 0.1%. For the determination of  $K$  under pressure, the pressure correction was made for the value of  $\eta$ <sup>21</sup> and  $\epsilon$ <sup>22</sup> appeared in the Onsager parameters and for the density of water,<sup>23</sup> which is necessary, together with  $\epsilon$ , for the calculation of the activity coefficient. The density data<sup>23</sup> were also used to correct the concentration in molarity.

Figures 2 and 3 show the final plot of eq 5 for nickel(II) succinate and nickel(II) maleate, respectively. The values of  $K$  determined from these plots are summarized in Table I. The present result for the stability constant of nickel(II) succinate at 1  $\text{kg cm}^{-2}$  is somewhat smaller than the value in the literature<sup>24</sup> ( $K = 194 \text{ mol}^{-1} \text{dm}^3$  at 15 °C and  $\mu \rightarrow 0$ ).

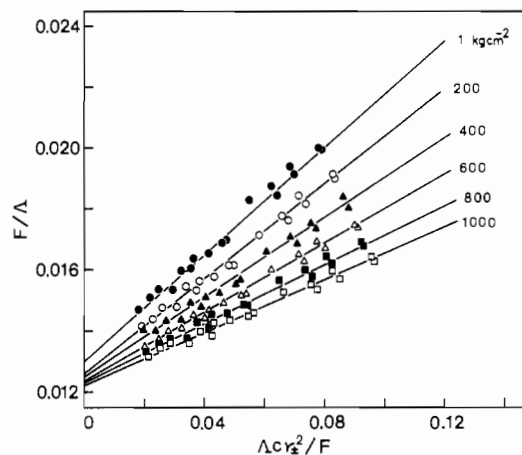


Figure 3. Plot of conductivity data according to eq 5 for nickel(II) maleate at 10 °C. Pressures ( $\text{kg cm}^{-2}$ ) are 1 (●), 200 (○), 400 (▲), 600 (△), 800 (■), and 1000 (□).

However, when the difference in temperature and the method applied is taken into account, the agreement may be regarded as satisfactory. For the stability constant of nickel(II) maleate at 1  $\text{kg cm}^{-2}$ , the available literature value<sup>24</sup> is  $K = 100 \text{ mol}^{-1} \text{dm}^3$  at 25 °C and  $\mu = 0.1$ . From this value, the stability constant at zero ionic strength is estimated to be  $660 \text{ mol}^{-1} \text{dm}^3$  by using the activity coefficient calculated from the Davies equation<sup>25</sup> ( $\gamma_{\pm} \approx 0.39$  for a divalent electrolyte at  $\mu = 0.1$ ), and this is comparable to the present result.

The pressure dependence of the stability constant leads to an evaluation of the reaction volume for the complex formation according to the relation<sup>5a</sup>

$$RT \left( \frac{\partial \ln K}{\partial P} \right)_T = -\Delta V^\circ + \sum \nu_i (RT \kappa_0) \quad (6)$$

where  $\Delta V^\circ$  is the change in the partial molar volume at infinite dilution accompanied by the complex formation from the metal ion and the ligand,  $\nu_i$  the stoichiometric coefficient of component  $i$ , and  $\kappa_0$  the solution compressibility. The second term in the right hand side of eq 6 is the correction term for the compression, which is required in the case of the molarity scale being used. For the present systems,  $\sum \nu_i = -1$  and  $RT \kappa_0 \approx 1.1 \text{ cm}^3 \text{mol}^{-1}$ . Figure 4a shows a plot of  $\log K$  against pressure. As is seen in this figure,  $\log K$  varies linearly with pressure in the studied pressure range. From the slope of the straight line fitted by a linear least-squares method, the reaction volume was determined according to eq 6. The results were  $\Delta V^\circ = 11.1 \pm 0.9 \text{ cm}^3 \text{mol}^{-1}$  for nickel(II) succinate and  $\Delta V^\circ = 14.9 \pm 0.4 \text{ cm}^3 \text{mol}^{-1}$  for nickel(II) maleate.

**Kinetic Study.** The rate constants for the complex-formation reaction were determined from the  $P$ -jump relaxation data. For the reaction represented by Scheme I, the reciprocal relaxation time is given by the expression

$$1/\tau = k_f \gamma_{\pm}^2 (c_{\text{Ni}} + c_{\text{L}}) + k_d \quad (7)$$

where  $k_f$  and  $k_d$  are the rate constants of the complex formation and the dissociation at zero ionic strength,  $c_{\text{Ni}}$  and  $c_{\text{L}}$  are the equilibrium concentration of the nickel(II) and ligand

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**Table II.** Relaxation Times and Rate Constants for Complex Formation at 10 °C and  $\mu \rightarrow 0$ 

$P/\text{kg cm}^{-2}$	$c^a/10^{-3}$ $\text{mol dm}^{-3}$	$c_{\text{Ni}} = c_{\text{T}}/10^{-3}$ $\text{mol dm}^{-3}$	$\gamma_{\pm}$	$1/\tau/10^3$ $\text{s}^{-1}$	$k_f/10^5$ $\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$
(a) Nickel(II) Succinate					
1	6.66	5.34	0.57	1.61	1.54
	8.32	6.53	0.54	1.62	1.50
	10.0	7.71	0.52	1.63	1.46
	11.6	8.82	0.50	1.67	1.46
	13.3	9.97	0.48	1.70	1.46
	15.0	11.11	0.47	1.73	1.46
	16.6	12.17	0.46	1.78	1.48
	18.3	13.29	0.45	1.80	1.47
	20.8	14.91	0.43	1.74	1.39
				av 1.47	
1000	2.50	2.38	0.68	0.987	0.704
	4.16	3.84	0.63	1.07	0.723
	6.66	5.96	0.57	1.27	0.811
	8.32	7.33	0.54	1.26	0.783
	10.0	8.69	0.52	1.23	0.745
	11.6	9.97	0.50	1.27	0.755
	13.3	11.31	0.48	1.41	0.828
	15.0	12.64	0.47	1.38	0.796
	16.6	13.88	0.46	1.44	0.822
	18.3	15.19	0.44	1.38	0.773
	20.8	17.09	0.43	1.45	0.799
				av 0.776	
(b) Nickel(II) Maleate					
1	1.74	1.26	0.74	0.967	2.98
	2.62	1.78	0.70	1.06	2.92
	3.49	2.24	0.68	1.14	2.90
	4.36	2.68	0.66	1.15	2.75
	5.23	3.11	0.64	1.25	2.85
	6.10	3.51	0.62	1.32	2.87
	6.98	3.91	0.61	1.25	2.63
	7.85	4.29	0.60	1.27	2.57
	8.72	4.67	0.59	1.41	2.78
				av 2.81	
1000	2.62	2.11	0.70	0.884	1.58
	3.49	2.71	0.67	0.934	1.57
	4.36	3.28	0.64	0.957	1.53
	5.23	3.83	0.63	0.991	1.51
	6.10	4.36	0.61	1.03	1.51
	6.98	4.89	0.59	1.07	1.53
	7.85	5.39	0.58	1.10	1.53
	8.72	5.89	0.57	1.18	1.60
	9.59	6.38	0.56	1.21	1.61
				av 1.55	

<sup>a</sup> Analytical concentration under atmospheric pressure.

ions, and  $\gamma_{\pm}$  is the mean activity coefficient of the free ions at a given ionic strength. With an independently determined stability constant, eq 7 is rewritten as

$$1/\tau = k_f[\gamma_{\pm}^2(c_{\text{Ni}} + c_{\text{L}}) + 1/K] \quad (8)$$

The bracketed term in eq 8 can be calculated from the stability constant data.

The values of  $k_f$  were determined from the relaxation time according to eq 8, where the equilibrium concentration and the mean activity coefficient were calculated from the stability constant by using an iteration procedure until  $\gamma_{\pm}$  converged to a constant value.  $\gamma_{\pm}$  was calculated according to the Davies equation<sup>25</sup> instead of the Debye-Hückel equation, since rather concentrated solutions were employed for kinetic measurements. Necessary pressure corrections were also made for the case under pressure as in an equilibrium study. Some examples of the obtained results are shown in Table II. The dissociation rate constants of the complex were determined from the relation

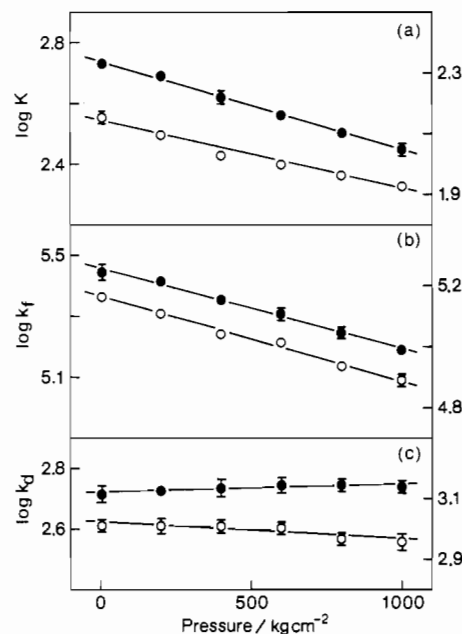
$$k_d = k_f/K \quad (9)$$

The values of the rate constants thus obtained are summarized in Table III.

**Table III.** Rate Constants as a Function of Pressure at 10 °C and  $\mu \rightarrow 0^a$ 

$P/\text{kg cm}^{-2}$	nickel(II) succinate		nickel(II) maleate	
	$k_f/10^5$ $\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$	$k_d/10^2 \text{ s}^{-1}$	$k_f/10^5$ $\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$	$k_d/10^2 \text{ s}^{-1}$
1	1.47 (0.04)	10.3 (0.5)	2.81 (0.14)	5.2 (0.3)
200	1.29 (0.06)	10.3 (0.6)	2.61 (0.06)	5.3 (0.2)
400	1.10 (0.03)	10.3 (0.5)	2.26 (0.08)	5.4 (0.3)
600	1.04 (0.03)	10.2 (0.5)	2.04 (0.10)	5.6 (0.3)
800	0.86 (0.03)	9.3 (0.4)	1.77 (0.06)	5.6 (0.3)
1000	0.78 (0.04)	9.2 (0.6)	1.55 (0.04)	5.5 (0.2)

<sup>a</sup> Standard deviations estimated from the values obtained at 9–11 different concentrations are shown in parentheses.



**Figure 4.** Pressure dependence of (a)  $\log K$ , (b)  $\log k_f$ , and (c)  $\log k_d$  at 10 °C:  $\circ$ , nickel(II) succinate (left scale);  $\bullet$ , nickel(II) maleate (right scale). Solid lines show the linear least-squares fits to the data points.

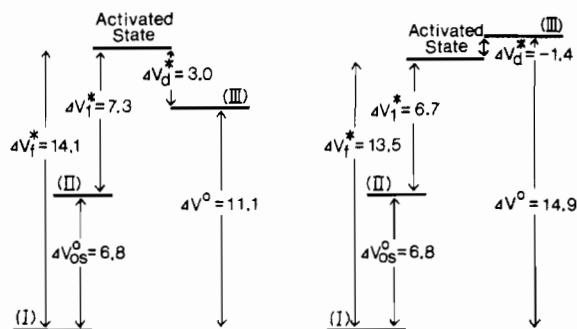
From the pressure dependence of the rate constants, the activation volume of the reaction can be estimated according to the relation analogous to eq 6<sup>5</sup>

$$RT \left( \frac{\partial \ln k}{\partial P} \right)_T = -\Delta V^* + \sum \nu_i (RT \kappa_0) \quad (10)$$

where  $\Delta V^*$  is the difference in the partial molar volumes of the transition state and the initial state, and  $\sum \nu_i$  corresponds to the difference in the molecularity of the two states. In Figure 4b,c  $\log k_f$  and  $\log k_d$  are plotted as a function of pressure. In general it is found that a plot of  $\log k$  against pressure is curved presumably due to the different compressibilities of the transition state and the initial state.<sup>5</sup> It has been shown that a parabolic relation of the form  $\log k = a + bP + cP^2$  frequently gives a good fit to the data.<sup>5</sup> In the present case, however, there was little apparent curvature, and hence a linear relation was fitted to the data by a least-squares method. From the slope of the straight line, the values of the activation volume for the complex formation ( $\Delta V_f^*$ ) and dissociation ( $\Delta V_d^*$ ) were determined according to eq 10. The results are as follows:  $\Delta V_f^* = 14.1 \pm 0.8 \text{ cm}^3 \text{ mol}^{-1}$  and  $\Delta V_d^* = 3.0 \pm 0.9 \text{ cm}^3 \text{ mol}^{-1}$  for nickel(II) succinate;  $\Delta V_f^* = 13.5 \pm 0.6 \text{ cm}^3 \text{ mol}^{-1}$  and  $\Delta V_d^* = -1.4 \pm 0.4 \text{ cm}^3 \text{ mol}^{-1}$  for nickel(II) maleate.

## Discussion

Volume profiles for the complex-formation reaction of nickel(II) succinate and nickel(II) maleate are shown in Figure

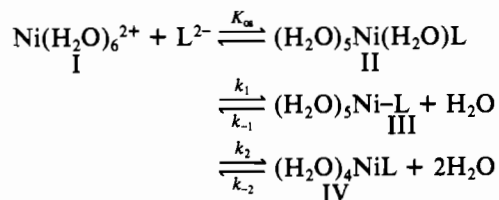


**Figure 5.** Volume profiles for the complex-formation reaction of nickel(II) succinate (left) and nickel(II) maleate (right). I, II, and III correspond to the compounds in Scheme III. The values of volume change in  $\text{cm}^3 \text{mol}^{-1}$  are shown in the figure.  $\Delta V_{0s}^\circ$  was calculated according to eq 18 (see text).

5. A remarkable feature in this figure is that the activation volumes for the complex formation are almost the same for the two systems, while an appreciable difference is seen in reaction volume.

The complex-formation reaction is generally understood in terms of the Eigen mechanism.<sup>1</sup> For a chelate complex between the nickel(II) ion and a bidentate ligand, this mechanism may be represented by Scheme II, where I is the free ion, II

#### Scheme II



is the outer-sphere complex, III is the monodentate complex with one end of the ligand left free, IV is the bidentate chelate complex,  $K_{0s}$  is the outer-sphere complex formation constant, and  $k$ 's are the rate constants of each step. If the complex is present as a stable bidentate chelate, the overall rate constants are related to the rate constants of each step in Scheme II by eq 11 and 12, under the assumption that  $\text{I} \rightleftharpoons \text{II}$  is very

$$k_f = K_{0s}k_1 \left( \frac{k_2}{k_2 + k_{-1}} \right) \quad (11)$$

$$k_d = k_{-1} \left( \frac{k_{-2}}{k_2 + k_{-1}} \right) \quad (12)$$

rapid compared with other steps and the intermediate III is in a steady state. Furthermore, two limiting cases are considered depending on the ratio of  $k_2/k_{-1}$ . (i) If  $k_2 \gg k_{-1}$ , then

$$k_f = K_{0s}k_1 \quad k_d = k_{-1}/K_2 \quad (13)$$

where  $K_2 = k_2/k_{-2}$ . In this case, the overall rate of chelate formation is determined by the rate of first bond formation between the metal ion and the ligand. (ii) If  $k_2 \ll k_{-1}$ , then

$$k_f = K_{0s}K_1k_2 \quad k_d = k_{-2} \quad (14)$$

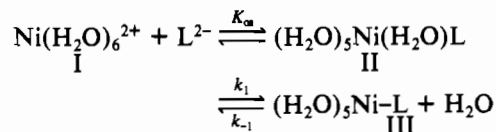
where  $K_1 = k_1/k_{-1}$ . The rate-determining step in this case is the chelate-ring-closure process.

Kinetics for the complex formation of the nickel(II) dicarboxylate have been frequently discussed on the basis of either of two assumptions described above. However, Yasunaga et al.<sup>16,26</sup> have pointed out that the complex with the relatively large  $k_d$  value ( $k_d \sim 10^3 \text{ s}^{-1}$ ) should be monodentate as the stable form rather than a chelate complex, since the large  $k_d$  value is in conflict with the requirement for stable chelate formation ( $k_2 \gg k_{-2}$ ) as is seen by examining eq 13

and 14. It has been considered that in this group are included the complexes with succinate,<sup>16</sup> maleate,<sup>16</sup> phthalate,<sup>26</sup> glutarate,<sup>27</sup> and adipate.<sup>28</sup> The reaction volume of the complex formation of nickel(II) succinate and of nickel(II) glutarate ( $\Delta V^\circ = 10.4 \pm 0.8 \text{ cm}^3 \text{mol}^{-1}$ <sup>29</sup>) is considerably smaller than those obtained for the bidentate chelate complexes ( $\Delta V^\circ = 14\text{--}18 \text{ cm}^3 \text{mol}^{-1}$ <sup>30</sup>). The positive reaction volume associated with such reactions under consideration may be ascribed partly to the elimination of solvated water around the coordinating group due to the coordination bond formation, which produces the free water and resultant volume increase, in addition to the release of electrostriction due to charge neutralization. Hence, smaller  $\Delta V^\circ$  values for nickel(II) succinate and nickel(II) glutarate coincide with monodentate complex formation rather than chelate complex formation. On the other hand,  $\Delta V^\circ$  of nickel(II) maleate is fairly larger than that of nickel(II) succinate and is comparable to those of chelate complexes. This difference may be attributed to the difference in the position occupied by the free carboxyl group in the monodentate complex. In nickel(II) maleate, the free carboxyl group should be restricted close to the nickel(II) ion, probably inside the outer sphere, due to the fixed structure imposed by the double bond, while in nickel(II) succinate, the free carboxyl group may be far from the nickel(II) ion. It seems likely that the close contact of the nickel(II) ion and the free carboxyl group reduces the degree of solvation of the complex as a whole and causes an excess volume increase for nickel(II) maleate.

If the concentration of the chelate complex is negligibly small compared with that of the monodentate species, Scheme II can be simplified to Scheme III. In this case, the overall

#### Scheme III



rate constants are expressed by eq 15 and 16. According to

$$k_f = K_{0s}k_1 \quad (15)$$

$$k_d = k_{-1} \quad (16)$$

eq 15, the experimentally measured activation volume for the complex formation is in fact a composite quantity expressed as

$$\Delta V_f^* = \Delta V_{0s}^\circ + \Delta V_1^* \quad (17)$$

where  $\Delta V_{0s}^\circ$  is the reaction volume for the outer-sphere complex formation and  $\Delta V_1^*$  is the activation volume for the bond formation. Therefore, in order to interpret  $\Delta V_f^*$ , it is necessary to take account of  $\Delta V_{0s}^\circ$ .

Hemmes<sup>31</sup> has shown that the volume change associated with ionic association can be estimated by the expression

$$\Delta V = RT \left[ \frac{|z_+z_-|e^2}{\epsilon kT} \left( \frac{\partial \ln \epsilon}{\partial P} \right)_T - \kappa_0 \right] \quad (18)$$

where  $z_+e$  and  $z_-e$  are the charges on the two ions and other symbols have their usual meanings. This expression has been derived by taking the pressure derivative of the Fuoss equation<sup>32</sup> and describes the volume change resulting from the

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release of the electrostriction due to charge neutralization. Equation 18 has been frequently used to estimate the value of  $\Delta V_{os}^\circ$ .<sup>14</sup> For the present systems,  $\Delta V_{os}^\circ$  was calculated to be  $6.8 \text{ cm}^3 \text{ mol}^{-1}$  from eq 18 by assuming  $a = 5 \text{ \AA}$  and by using  $(\partial \ln \epsilon / \partial P)_T = 59 \times 10^{-6} \text{ kg}^{-1} \text{ cm}^2$  (see ref 14). Hence, the values of  $\Delta V_1^*$  are estimated to be  $7.3 \pm 0.8 \text{ cm}^3 \text{ mol}^{-1}$  for nickel(II) succinate and  $6.7 \pm 0.6 \text{ cm}^3 \text{ mol}^{-1}$  for nickel(II) maleate. These values show a close resemblance to the activation volume of the water exchange of the aquonickel(II)

ion,  $\Delta V_{H_2O}^* = 7.2 \pm 0.3 \text{ cm}^3 \text{ mol}^{-1}$ , obtained from a high-pressure NMR study.<sup>34</sup> This fact indicates that the rate-determining step is the loss of water from the inner coordination shell of the nickel(II) ion and provides further support for the validity of the Eigen mechanism in the present systems.

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**Registry No.** Nickel, 7440-02-0; succinic acid, 110-15-6; maleic acid, 110-16-7.

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## Kinetic and Equilibrium Studies of Complex Formation of Nickel(II) with Carboxylate Ligands at High Pressure. 2. Nickel(II) Glycolate and Nickel(II) Lactate

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Kinetic and equilibrium measurements were carried out for the complexation reactions of nickel(II) glycolate and nickel(II) lactate in water at pressures up to  $1000 \text{ kg cm}^{-2}$ . The reaction volume,  $\Delta V^\circ$ , and the activation volume,  $\Delta V_1^*$ , for the complexation reaction were estimated from the pressure dependence of the stability constant and the rate constant as follows:  $\Delta V^\circ = 17.3 \pm 1.0 \text{ cm}^3 \text{ mol}^{-1}$  and  $\Delta V_1^* = 14.7 \pm 0.5 \text{ cm}^3 \text{ mol}^{-1}$  for nickel(II) glycolate;  $\Delta V^\circ = 17.6 \pm 0.9 \text{ cm}^3 \text{ mol}^{-1}$  and  $\Delta V_1^* = 13.5 \pm 0.4 \text{ cm}^3 \text{ mol}^{-1}$  for nickel(II) lactate. After correction for the volume change associated with the outer-sphere complex formation ( $\Delta V_{os}^\circ = 3.1 \text{ cm}^3 \text{ mol}^{-1}$ ), these activation volumes were consistent with the mechanism previously proposed by Yasunaga et al., where the rate-determining step was assigned to the chelate-ring-closure step. Furthermore, with the aid of the reaction volume for the monodentate complex with succinic acid, the volume profiles for the complexation reaction were obtained, on which some discussions were given.

### Introduction

It has been well recognized that the activation volume is a useful parameter for the elucidation of reaction mechanisms.<sup>1</sup> Recently, various apparatus capable of measuring rapid reaction at high pressure have been designed<sup>2-7</sup> and applied to the complexation reactions of labile metal ions.<sup>2,7-9</sup> We have been studying the kinetics and equilibrium of the complex formation between nickel(II) and a variety of carboxylate ligands under high pressure. In a previous paper,<sup>10</sup> we have reported the results obtained with nickel(II) succinate and nickel(II) maleate. The present paper is concerned with the kinetics and equilibrium of nickel(II) glycolate and nickel(II)

lactate complexation at various pressures up to  $1000 \text{ kg cm}^{-2}$ . Kinetics for the same systems at atmospheric pressure have already been studied by Yasunaga et al.,<sup>11,12</sup> and they assigned the rate-determining step of the overall complexation reaction to the chelate-ring closure through the hydroxyl group. The purpose of the present work is to obtain the volume profile for these reactions in order to elucidate the details of the reaction mechanism in terms of the volume change.

### Experimental Section

Stock solutions of nickel(II) glycolate and nickel(II) lactate were prepared by mixing  $\text{NiSO}_4$  and the respective acid in the molar ratio of 1:2, where the sulfate ion was precipitated out as  $\text{BaSO}_4$  by adding an equivalent amount of  $\text{Ba(OH)}_2$  solution. The concentrations of nickel(II) glycolate and nickel(II) lactate were determined by EDTA titration. Each sample solution was prepared by diluting the stock solution to the desired concentration. All the reagents except glycolic acid were of a guaranteed grade and were used without further purification. Glycolic acid was purified by recrystallization from acetone. The pH of the solution ranged from 5.9 to 6.1 and from 5.9 to 6.0 for nickel(II) glycolate and nickel(II) lactate, respectively. In these pH ranges, most of the ligands are in the dissociated form. Stability constants of the complexes were determined from conductivity measurements using the same apparatus as described in a previous paper.<sup>10</sup> Kinetic measurements were made by means of a high-pressure  $P$ -jump technique, which was described in some detail previously.<sup>7,10</sup> Figure 1 shows typical relaxation effects observed in

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