

Kinetic Studies of Co(II)-Malonate, Malate, and Glycolate Complex-formation Reactions in Aqueous Solutions by the Pressure-shock Method

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A pressure-shock apparatus applicable for the kinetic studies of rapid reactions in solution was constructed and used to study Co(II)-carboxylate complex-formation reactions. The chelate complex-formation reaction was interpreted in terms of a step-by-step mechanism, and the rate constants were obtained. The chelate-ring closing-and-opening process was revealed to be the rate-determining step.

For the model of the complex formation of bidentate ligands, a step-by-step mechanism has been proposed. When the complex is stable as a chelate complex, the rate-determining step has been assigned to either the first-bond formation-and-dissociation process^{1–6)} or the chelate-ring closing-and-opening process.^{7–9)} The purpose of the present work is to examine these assignments for the Co(II)-bidentate carboxylate complex-formation reactions. Although the equilibrium properties of the cobalt(II) carboxylates have been well studied,¹⁰⁾ few kinetic studies have been carried out.¹¹⁾ The reason may be that the reaction of cobalt-(II) ion with ligand is too fast to be studied by conventional techniques.

Another purpose is to test the applicabilities of our newly constructed pressure-shock apparatus. Even though the pressure-jump method¹²⁾ is one of the most useful techniques for the kinetic studies of very rapid reactions in solution, applications of this method have been limited to reactions with relaxation times greater than 100 μ s. This disadvantageous time constant has been improved by at least one order of magnitude by the pressure-shock method.^{13–15)}

Experimental

Apparatus. The pressure-shock apparatus constructed was a modification of that described by Platz and Hoffmann.¹⁵⁾ A schematic diagram is shown in Fig. 1. The experimental procedure is as follows. Nitrogen gas of 20 atm is introduced into the low pressure chamber (G). Next, the high-pressure N₂ gas is introduced into chamber (D). The increase of the pressure in chamber (D) bursts or shears out the metal diaphragm (E) at a definite pressure. The pressure-change takes at least 50 μ s. While the pressure wave propagates in the low-pressure gas in (G) and in the transmitting liquid (ethanol) (H), the wave front is sharpened and becomes a shock wave.¹⁶⁾ The shock wave is reflected at the bottom of the sample cell (K) and propagates back through the liquid, and an expansion wave is generated at the surface of the liquid; the latter wave cancels the exerted pressure. As a result, the pressure in the sample cell continues to be high until the shock-front returns to the sample cell. The duration of the high-pressure pulse can be varied by changing the liquid level. The relaxation effect was detected conductometrically by a high-frequency bridge of 1.2 MHz. From the pressure-shock trace obtained for a MnSO₄ solution, which exhibits a relaxation effect faster than 1 μ s (Fig. 2a), the time constant of the present apparatus was determined to be less than 4 μ s. The features of the pressure pulses for the MnSO₄ solution and the Co(II)-malonate

system are shown in Figs. 2b and 2c respectively. The temperature of the cell was controlled at 25.0 ± 0.3 °C by circulating thermostated water through a copper tube spiraled around the shock tube and the cell.

Higher-pressure shock waves can be obtained by increasing the burst pressure by using a thicker metal diaphragm or by the use of lower-molecular-weight gas in the high-pressure chamber and higher-molecular-weight gas in the low-pressure chamber.¹⁶⁾ Following the latter idea, we tried H₂ gas in the high-pressure chamber and obtained a pressure pulse several times larger than that obtained when N₂ gas was used. In the present experiments, however, N₂ gas was used throughout the measurements since H₂ gas is explosive and the advantage was not so remarkable.

Materials. Wako reagent-grade chemicals were used. Stock solutions of cobalt(II) carboxylates were prepared in the same way as those of nickel(II) carboxylates.^{4–6)} By

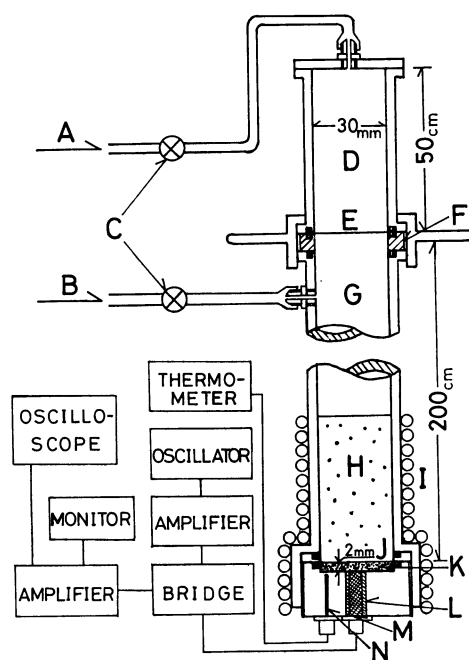


Fig. 1. The schematic diagram of the pressure-shock apparatus.

(A): High-pressure gas inlet, (B): low-pressure gas inlet, (C): electric solenoid valve, (D): high-pressure gas chamber, (E): metal diaphragm, (F): cutter, (G): low-pressure gas chamber, (H): transmitting liquid (ethanol), (I): thermostat tube, (J): polyethylene membrane, (K): sample cell, (L): insulator, (M): electrode, (N): thermistor.

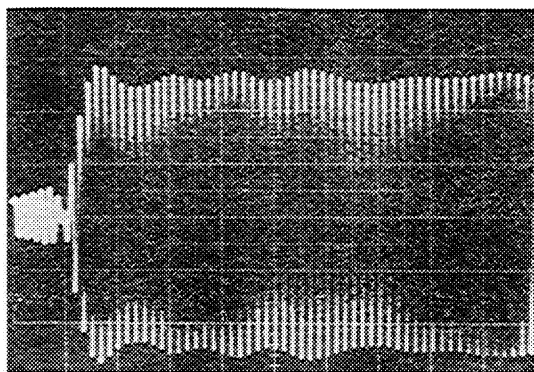


Fig. 2a. Pressure-shock trace obtained for 5×10^{-3} M MnSO_4 solution. Sweep: $5 \mu\text{s}/\text{div}$.

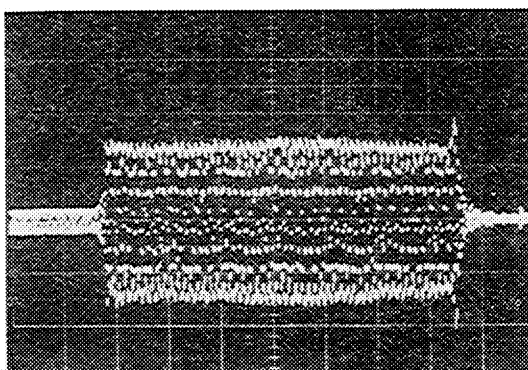


Fig. 2b. Whole features of the pressure-shock pulse. Sample: 5×10^{-3} M MnSO_4 , sweep: $200 \mu\text{s}/\text{div}$.

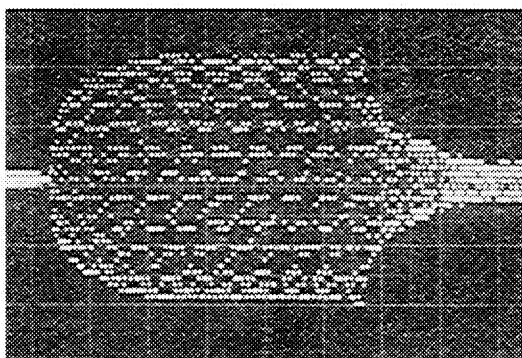


Fig. 2c. The relaxation spectra of Co(II)-malonate system. Concentration; 1×10^{-3} M, sweep: $50 \mu\text{s}/\text{div}$ at 25°C .

considering the hydrolysis of the cobalt(II) ion and the acid dissociation of the ligand, the proper value of the pH was determined; the pH was adjusted by the drop-by-drop addition of dilute nitric acid solution.

Results

The experimental conditions and the reciprocal relaxation times observed are shown in Table 1. The concentration dependence of the relaxation time is best explained by the following equilibria.

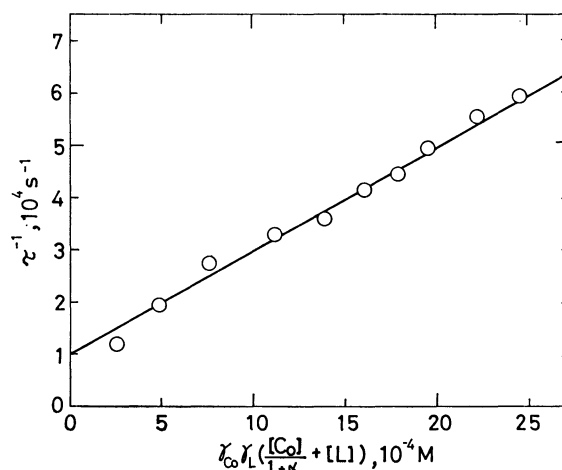
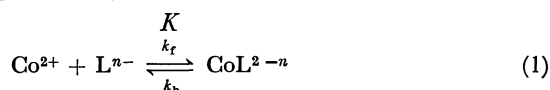
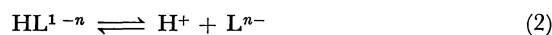
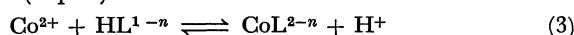


Fig. 3. τ^{-1} vs. $\gamma_{\text{Co}}\gamma_{\text{L}}\left(\frac{[\text{Co}]}{1+\alpha} + [\text{L}]\right)$ plot of Co(II)-malate system at 25°C .



($n=2$ for malonate and malate systems and 1 for glycolate system)

where L^{n-} is a dissociated ligand, HL^{1-n} is a mono-protonated ligand, CoL^{2-n} is a 1:1 complex, k_f and k_b are the rate constants, and $K(=k_f/k_b)$ is the stability constant. In the present pH ranges, the contributions of the complex formation with the monoprotated ligand (Eq. 3):



to the present relaxation phenomenon was neglected. Since the protonation of the carboxyl group (Eq. 2) is much faster than the complex formation reaction (Eq. 1), the relaxation time, τ , of Eq. 1 is expressed by the equation:

$$\tau^{-1} = k_f \cdot \frac{\gamma_{\text{Co}} \cdot \gamma_{\text{L}}}{\gamma_{\text{CoL}}^*} \cdot \left(\frac{[\text{Co}]}{1+\alpha} + [\text{L}] \right) + k_b \cdot \frac{\gamma_{\text{CoL}}}{\gamma_{\text{CoL}}^*} \quad (4)$$

with

$$\alpha = \frac{[\text{H}]}{K_a + [\text{L}]} \quad (5)$$

where γ_i is the activity coefficient of the i -th species, the brackets indicate the concentration, the superscript $*$ means the activated complex, K_a is the acid dissociation constant of the (second) carboxyl group, and charges are omitted for the sake of convenience. On the assumptions that the activity coefficient of a noncharged complex is unity, $\gamma_{\text{CoL}} = \gamma_{\text{CoL}}^*$, and $\gamma_{\text{CoL}}^* = \gamma_{\text{L}}^-$, Eq. 4 is rewritten in the form:

$$\tau^{-1} = F(C) \cdot k_f + k_b \quad (6)$$

where $F(C)$ is the concentration term including the activity coefficient term. Calculations of the activity coefficients were performed using the Davies equation.¹⁷⁾

Evaluation of the rate parameters was carried out as follows. First, the concentrations of the species in solution were calculated from the stability constant, K , which is available in the literature. Then, the τ^{-1} values were plotted against $F(C)$ to give k_f and k_b from the slope and the intercept of the straight line respectively. The ratio of k_f and k_b gives a so-called kinetical-

TABLE 1. EXPERIMENTAL CONDITIONS AND τ^{-1} VALUES OF THE COBALT(II) CARBOXYLATES AT 25.0 °C

Malonate			Malate			Glycolate		
ΣC^a (10^{-4} M)	pH	τ^{-1} ^{b)} (10^4 s $^{-1}$)	ΣC^a (10^{-4} M)	pH	τ^{-1} ^{b)} (10^4 s $^{-1}$)	ΣC^a (10^{-4} M)	pH	τ^{-1} ^{b)} (10^4 s $^{-1}$)
1.5	6.43	0.9 \pm 0.3	2.0	6.56	1.2 \pm 0.1	5.0	5.75	5.4 \pm 0.2
2.0	6.49	0.9 \pm 0.1	5.0	6.55	2.0 \pm 0.1	10	5.87	5.7 \pm 0.8
5.0	6.57	2.0 \pm 0.4	10	6.49	2.7 \pm 0.2	20	5.97	7.2 \pm 0.3
7.5	6.59	2.0 \pm 0.2	20	6.39	3.3 \pm 0.2	40	6.07	8.1 \pm 0.6
10	6.60	2.5 \pm 0.2	30	6.54	3.6 \pm 0.3	60	6.14	9.0 \pm 0.7
20	6.60	3.3 \pm 0.3	40	6.50	4.2 \pm 0.4	80	6.16	10.3 \pm 0.7
40	6.51	4.4 \pm 0.9	50	6.59	4.4 \pm 0.3	100	6.17	11.5 \pm 0.9
60	6.45	4.6 \pm 0.2	60	6.56	5.0 \pm 0.3			
80	6.39	5.2 \pm 0.6	80	6.29	5.6 \pm 0.2			
100	6.37	6.0 \pm 1.6	100	6.40	6.0 \pm 0.4			

a) Overall concentration of the Cobalt(II) carboxylates. b) Mean value of at least seven experiments.

TABLE 2. RATE AND EQUILIBRIUM CONSTANTS OF Co(II) COMPLEX-FORMATION REACTION (I) AT 25 °C AND $\mu \rightarrow 0$

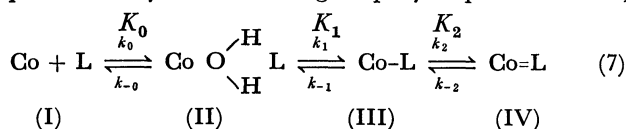
Ligand	Malonate	Malate	Glycolate
k_f , M $^{-1}$ s $^{-1}$	2.7 (± 0.1) $\times 10^7$	2.1 (± 0.1) $\times 10^7$	6.0 (± 0.3) $\times 10^6$
k_b , s $^{-1}$	6.1 (± 2.5) $\times 10^3$	8.9 (± 1.5) $\times 10^3$	4.6 (± 0.3) $\times 10^4$
log K	3.6 (± 0.3)	3.4 (± 0.1)	2.1 (± 0.1)
log K^a	3.60 ¹⁸⁾	3.00 ¹⁸⁾	1.96 ¹⁹⁾

a) Literature value.

ly determined K which should coincide with the foregoing K value used for the calculation of $F(C)$. If they did not coincide, the kinetically obtained K was used for the calculation of $F(C)$ and the τ^{-1} vs. $F(C)$ plot was again drawn. The above procedures were repeated until a self-consistent K value was obtained. The final plot of the Co(II)–malate system is shown in Fig. 3 as an example. The values of k_f , k_b , and K are listed in Table 2, along with the literature value of K .^{18,19)} The values of K obtained kinetically are in satisfactory agreement with those in the literature.

Discussion

The ligands used in the present experiment are known to make stable chelate complexes with cobalt(II) ion. The chelate complex-formation reaction is represented by the following step-by-step mechanism,



where (I) represents free ions; (II), an ion-pair; (III), a monodentate complex; and (IV), a chelate complex.

Kinetic studies of the chelate-complex formation of bidentate carboxylates have been widely carried out for the nickel(II) complexes. In these studies, the rate-determining step of the complex formation has been ascribed to either the first-bond formation-and-dissociation process, (II) \rightleftharpoons (III),¹⁻⁶⁾ or the chelate-ring closing-and-opening process, (III) \rightleftharpoons (IV).⁷⁻⁹⁾ In the former concept, the following problems remain unsolved. The values of k_1 obtained from the assumed

equation $k_f = k_0 \cdot k_1$, have been regarded as equal to the water-exchange rate constant of the metal ion, $k_{\text{H}_2\text{O}}$.²⁰⁾ However, the consistency has not been necessarily satisfactory, and the k_1 's have occasionally been one order of magnitude smaller than $k_{\text{H}_2\text{O}}$. Also, even if $k_1 = k_{\text{H}_2\text{O}}$ could be satisfied, the assumption that $k_2 \gg k_1$ is dubious, because the water-substitution process is also involved in the chelate-ring-closing step, and k_2 cannot exceed $k_{\text{H}_2\text{O}}$ ($=k_1$). The above reasons led us to adopt the second concept in the present study.

On the assumption that the intermediate species, (II) and (III), are in a steady state, the rate constants in Eq. 7 are related to the overall rate constants, k_f and k_b , by the following equations:

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

$$k_b = k_{-2} \left(\frac{k_{-1}}{k_2 + k_{-1}} \right). \quad (9)$$

The equilibrium and kinetic parameters in these equations were evaluated as follows.

K_0 was estimated theoretically by the Fuoss equation:²¹⁾

$$K_0 = \frac{4\pi N a^3}{3000} \cdot e^{-U(a)/kT} \quad (10)$$

where N is Avogadro's number, a is the distance of the closest approach of two ions, which was assumed to be 8 \AA ,²²⁾ and $U(a)$ is a Coulomb-energy term. K_0 at $\mu \rightarrow 0$ was calculated to be 46 M^{-1} for the malonate and malate systems and 7.7 M^{-1} for the glycolate system.

The value of k_1 was assumed to be equal to that of the $k_{\text{H}_2\text{O}}$ of the cobalt(II) ion, i.e., $k_{\text{H}_2\text{O}} = 2.6 \times 10^6$

s⁻¹.²³⁾ This assumption may be made because, in many monodentate complex-formation reactions, the rate-determining step has been revealed to be a water-dissociation process from the coordination site of the metal ion, irrespective of the entering ligand.

The value of k_{-1} was estimated from the pK_a value of the ligand. In the kinetic studies of the complex formation reactions of nickel(II) dicarboxylates, Hoffmann has estimated the k_{-1} value from the following experimental relationship between $\log k_{-1}$ and pK_a for each of the ligands:⁷⁻⁹⁾

$$\log k_{-1} = -0.22 pK_a + A \quad (A = \text{constant}). \quad (11)$$

Unfortunately, however, the same relationship has not been established for the cobalt(II) complexes because of the lack of the kinetic data. Thus, in the present case, the k_{-1} of the Co(II)-acetate system was estimated first. Since acetate makes only monodentate complexes, and a reliable stability constant is given in the literature, the k_{-1} can be estimated. First, the stability constant, K , of the acetate complex is related to the equilibrium and rate constants of each step by the equation:

$$K = K_0 (1 + K_1) = K_0 \left(1 + \frac{k_1}{k_{-1}} \right) \quad (12)$$

where K_0 , K_1 , k_1 , and k_{-1} are the same as in Eq. 7. By employing the values of $K = 10^{1.29} \text{ M}^{-1}$,¹⁹⁾ $K_0 = 7.7 \text{ M}^{-1}$, and $k_1 = 2.6 \times 10^6 \text{ s}^{-1}$, the k_{-1} of the acetate system ($pK_a = 4.75$) was calculated to be $1.7 \times 10^6 \text{ s}^{-1}$. Then, applying Eq. 11 to the Co(II)-carboxylate system, the k_{-1} value of each system was estimated from the value of the pK_a of the ligand; *i.e.*, by the use of the values for the acetate system, we obtain:

$$\log (k_{-1}/1.7 \times 10^6) = -0.22 (pK_a - 4.75). \quad (13)$$

The calculated values of k_{-1} and $K_1 (= k_1/k_{-1})$ are listed in Table 3, together with the pK_a values. By the use of the values of K_0 , k_1 , k_{-1} , k_f , and k_b , the values of k_2 and k_{-2} were calculated by Eqs. 8 and 9; these results are also listed in Table 3.

By comparing the values of the equilibrium and the rate parameters in Tables 2 and 3, we can deduce the following:

- (1) The complex is stable as a chelate complex rather than as a monodentate complex or an ion-pair.
- (2) The chelate-ring closing and opening reactions are the rate-determining processes of the complex

TABLE 3. EQUILIBRIUM AND RATE CONSTANTS OF THE STEP-BY-STEP COMPLEX-FORMATION REACTION (7) OF Co(II) CARBOXYLATE AT 25 °C AND $\mu \rightarrow 0$

Ligand	Malonate	Malate	Glycolate
pK_a of acid ^{a)}	5.69	5.11	3.83
K_0 , M^{-1}	46	46	7.7
K_1	2.4	1.8	1.0
K_2	40	28	17
k_1 , s^{-1}	2.6×10^6	2.6×10^6	2.6×10^6
k_{-1} , s^{-1}	1.1×10^6	1.4×10^6	2.7×10^6
k_2 , s^{-1}	3.2×10^5	3.0×10^5	1.2×10^6
k_{-2} , s^{-1}	7.9×10^3	1.1×10^4	6.6×10^4

a) Ref. 24.

formation and dissociation reactions respectively.

(3) The stability of the malonate complex relative to the others is due to the fact that it has the slowest rate of chelate-ring opening (k_{-2}). The malonate system has once been studied kinetically by the temperature-jump method.¹¹⁾ Compared with the temperature-jump data, the k_f value of the present work is three times larger, while the k_b value is two times smaller. These inconsistencies may be ascribed to the differences in either the experimental conditions, *e.g.*, the ionic strength, or the stability constants used for the calculations.

(4) The glycolate complex is one order of magnitude less stable than the others. This is explained by the natures of the ligands, *i.e.*, the electrostatic charge (reflected by K_0), the acidity of the carboxyl group (K_1), and the chelating groups (K_2). From the kinetic standpoint, the fastest chelate-ring-closing rate indicates that a five-membered chelate complex is preferable to the complex formation, while the very rapid chelate-ring-opening rate is due to a weak coordination of a hydroxyl group in comparison with the carboxyl group.

In the malate system, both the equilibrium and the kinetic parameters were close to the corresponding values of the malonate system, even though some differences had been expected from the structural differences of these ligands. Further details of the malate complex formation may be revealed by additional experiments on analogous ligand systems, *e.g.*, β -hydroxypropionate or succinate systems.

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