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Kinetics of the Reducing Reaction of the Tris(oxalato)cobaltate(III) Ion Induced by the Reaction between Copper(II) and Thiosulfate in Aqueous Solution

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Abstract

The kinetic study of the reducing reaction of the tris(oxalato)cobaltate(III) ion ($[Co(C_2O_4)_3]^{3-}$) induced by the reaction between the copper(II) and thiolsulfate ions has been made in an aqueous solution. The initial rate of the reducing reaction of the $[Co(C_2O_4)_3]^{3-}$ ion was proportional to the initial concentrations of the $[Co(C_2O_4)_3]^{3-}$ ion as well as the copper(II) ion, and was inversely proportional to those of the thiosulfate ion. The rate of the induced reducing-reaction of the $[Co(C_2O_4)_3]^{3-}$ ion was greatly retarded by the presence of complex-forming substances such as ethylenediaminetetraacetate and oxalate. The mechanism of reaction is presented to account for the results obtained, and the rate constant for the reaction between copper(I) and tris(oxalato)cobaltate(III) is determined and discussed by the term of the Marcus theory.

Introduction

The kinetic studies of the reducing reactions of the tris(oxalato)cobaltate(III) ion by the iron(II) ion [1–3] and by the chromium(II) ion [4] have been carried out by a number of researchers, whereas, those by the copper(I) ion have not been made until now. Kinetic studies of the electron-transfer reaction using the copper(I) ion are extremely scarce, owing to instability of the copper(I) ion with respect to molecular oxygen and to the ease of the disproportionation reaction of $2Cu^{I} \rightarrow Cu^{II} + Cu$.

The copper(II) ion undergoes a facile reduction to the copper(I) ion by the thiosulfate ion in aqueous solutions, and thus, the reaction between copper(II) and thiosulfate could induce the reducing reactions of the $[Co(C_2O_4)_3]^{3-}$ ion. In the present study we demonstrate the reducing reaction of the tris(oxalato)cobaltate(III) ion by the copper(I) ion which is produced homogeneously by the reaction between copper(II) and thiosulfate. The rate constant for the reaction $[Co(C_2O_4)_3]^{3-} + Cu^{I} \rightarrow Co^{II} + 3C_2O_4^{2-} + Cu^{II}$ will be determined and be discussed by the term of the Marcus theory [5].

Experimental

Chemicals

$K_3[Co(C_2O_4)_3]\cdot 6H_2O$ was synthesized following methods in the literature [6, 7]. Sodium thiosulfate and copper(II) sulfate of the guaranteed grade reagents were used without further purification. The other chemicals used were of the guaranteed grade reagents. The redistilled water used was prepared from the anion–cation exchange resin water by successive distillation from solutions with and without permanganate in a glass still.

Procedure

The reaction was, unless otherwise stated, initiated by mixing the copper(II) solution with a solution of tris(oxalato)cobaltate(III) and thiosulfate under the conditions given. The absorbance of the $[Co(C_2O_4)_3]^{3-}$ ion was measured at 604 and 425 nm using a Hitachi Model 100-40 spectrophotometer. The reaction vessel was covered with a black adhesive plastic tape to ensure darkness, and was placed in a thermostatted bath at 25 °C. Pure nitrogen gas was constantly bubbled through the reaction solution before as well as after initiating the induced reaction, and the aliquot samples were withdrawn at appropriate times to measure the absorbance of the $[Co(C_2O_4)_3]^{3-}$ ion.

Results

The reducing reaction of the $[Co(C_2O_4)_3]^{3-}$ ion by the thiosulfate ion did not occur at all under

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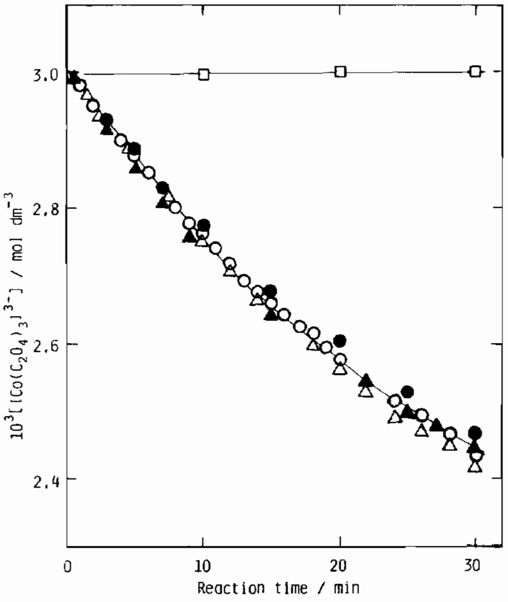

Fig. 1. Examples of kinetic runs. Conditions: 25 °C, pH 4.8–6.0, dark; the initial concentrations of tris(oxalato)cobaltate(III), copper(II), and thiosulfate ions are 0.003, 0.001, and 0.005 mol dm^{-3}, respectively. Reactions were initiated by adding the copper(II) solution into a solution containing $[Co(C_2O_4)_3]^{3-}$ and $S_2O_3{}^{2-}$ for ○ and ●, and by adding the $[Co(C_2O_4)_3]^{3-}$ solution into a solution containing thiosulfate and copper(II) ions which had stood for 20 min (▲) and for 1 h (△). Plots ● and ▲ indicate the runs in the absence of oxygen. Plots □ indicate results obtained in the absence of copper(II).

conditions of pH 4–6 at 25 °C, but it occurred dramatically following the addition of a small amount of the copper(II) ion into a solution containing the tris(oxalato)cobaltate(III) and thiosulfate ions. The representative kinetic runs are illustrated in Fig. 1. It is to be noted that the induced reducing reaction of the $[Co(C_2O_4)_3]^{3-}$ ion is not appreciably affected by the dissolved oxygen in solution.

Empirical Rate Law

The initial rate of the induced reducing reaction of the $[Co(C_2O_4)_3]^{3-}$ ion (V_i) was determined at various concentrations of reactants. The results obtained are given in Table I. The values of V_i were proportional to each concentration of the $[Co(C_2O_4)_3]^{3-}$ and copper(II) ions, and were inversely proportional to the thiosulfate ion concentration which was added initially (see Table I and Fig. 2). Consequently, the empirical rate law is described as follows.

$$-\frac{\Delta[[Co(C_2O_4)_3]^{3-}]_i}{\Delta t} = V_i$$

$$= \frac{k_{obs}[[Co(C_2O_4)_3]^{3-}]_i[Cu(II)]_i}{[S_2O_3{}^{2-}]_i} \qquad (1)$$

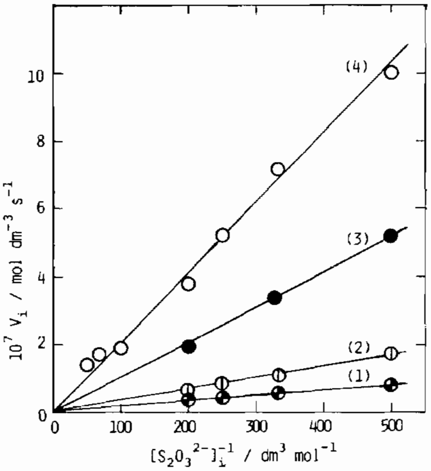

Fig. 2. Plots of V_i *vs.* $[S_2O_3]_i^{-1}$ (eqn. (1)). Initial concentrations: 1×10^{-4}, 2×10^{-4}, 5×10^{-4}, and 1×10^{-3} mol dm^{-3} in copper(II) sulfate for lines (1), (2), (3), and (4), respectively; 3×10^{-3} mol dm^{-3} in potassium tris(oxalato)cobaltate(III); and varied concentrations of the thiosulfate ion. Other conditions are the same as those in Table I.

where suffix i indicates the initial stage of reaction and the initial concentrations are assumed to be equal to those added initially, *i.e.*, at $t = 0$, and k_{obs} is the rate constant to be determined empirically by using eqn. (1).

Mechanism of Reaction

The results obtained could be accounted for by the following reactions.

$$2S_2O_3{}^{2-} + 2Cu^{II} \overset{K}{\rightleftharpoons} 2Cu^{I} + S_4O_6{}^{2-} \qquad (2)$$

$$Cu^{I} + S_2O_3{}^{2-} \overset{K_1}{\rightleftharpoons} [Cu(S_2O_3)]^{-} \qquad (3)$$

$$[Cu(S_2O_3)]^{-} + S_2O_3{}^{2-} \overset{K_2}{\rightleftharpoons} [Cu(S_2O_3)_2]^{3-} \qquad (4)$$

$$[Co(C_2O_4)_3]^{3-} + Cu^{I} \xrightarrow{k} Co^{II} + 3C_2O_4{}^{2-} + Cu^{II} \qquad (5)$$

where Cu^I, Cu^{II}, and Co^{II} indicate all the forms of the corresponding oxidation states, and are, however, the aquated species dominantly in solution at least for the initial stages of reaction. The concentration of the copper(II) ion added is described as follows.

$$[Cu(II)]_{added} = [Cu^{II}] + [[Cu(S_2O_3)]^{-}] + [[Cu(S_2O_3)_2]^{3-}] + [Cu^{I}] \qquad (6)$$

Thus, concentrations of the univalent copper(I) ion are described as follows

TABLE I. Values of V_i and k_{obs} in eqn. (1) under Various Conditions[a]

$10^3[[Co(C_2O_4)_3]^{3-}]_i$ (mol dm^{-3})	$10^3[Cu(II)]_i$ (mol dm^{-3})	$10^3[S_2O_3^{2-}]_i$ (mol dm^{-3})	$10^7\ V_i$ (mol dm^{-3} s^{-1})	$10^4\ k_{obs}$ (s^{-1})
1.0	1.0	10	0.59	5.9
2.0	1.0	10	1.3	6.5
3.0	1.0	10	1.9 1.9^b	6.3 6.3^b
4.0	1.0	10	2.4	6.0
10.0	1.0	10	6.8	6.8
3.0	0.10	5.0	0.34^b	5.7^b
3.0	0.20	5.0	0.68^b	5.7^b
3.0	0.40	5.0	1.50^b	6.3^b
3.0	0.50	5.0	2.0 2.0^b	6.7 6.7^b
3.0	1.0	5.0	3.8 4.1^b 3.7^c	6.3 6.8^b 6.2^c
3.0	1.0	4.0	5.3	7.1
3.0	1.0	3.0	7.2	7.2
3.0	1.0	2.0	10	6.7
3.0	1.0	1.0	22	7.3
3.0	1.0	10	1.9	6.3
3.0	0.50	2.0	5.2^b	6.9^b
3.0	0.50	3.0	3.4^b	6.8^b
3.0	0.50	4.0	2.5^b	6.7^b
3.0	0.20	1.0	3.6^b	6.0^b
3.0	0.20	2.0	1.8^b	6.0^b
3.0	0.20	3.0	1.1^b	5.5^b
3.0	0.20	4.0	0.91^b	6.1^b
3.0	0.10	1.0	1.30^b	4.3^b
3.0	0.10	2.0	0.76^b	5.1^b
3.0	0.10	3.0	0.57^b	5.7^b
3.0	0.10	4.0	0.42^b	5.6^b
			average	6.3 ± 0.6

[a] Reactions were initiated by adding the copper(II) solution into a solution containing the $[Co(C_2O_4)_3]^{3-}$ and thiosulfate ions. Other conditions are the same as those in Fig. 1. [b] As in [a], but reactions were initiated by adding the $[Co(C_2O_4)_3]^{3-}$ ion into a solution containing the thiolsulfate and copper(II) ions which had stood for 60 min. [c] As in [a], but in the absence of oxygen.

$$[Cu^I] = \frac{[Cu(II)]_{added}}{1 + K_1[S_2O_3^{2-}] + K_1K_2[S_2O_3^{2-}]^2 + [S_4O_6^{2-}]^{1/2}/(K^{1/2}[S_2O_3^{2-}])} \tag{7}$$

K_1 and K_2 have been reported to be 2.24×10^{10} and 83 dm^3 mol^{-1}, respectively [8], and K is evaluated to be 300 dm^3 mol^{-1} by using the standard redox potentials of 0.08 and 0.153 V for $S_2O_3^{2-}/S_4O_6^{2-}$ and for Cu^{2+}/Cu^+, respectively [9]. Accordingly, the rate of the reducing reaction of the $[Co(C_2O_4)_3]^{3-}$ ion can be described by eqn. (8)

$$-\frac{d[[Co(C_2O_4)_3]^{3-}]}{dt} = k[[Co(C_2O_4)_3]^{3-}][Cu^I]$$

$$= \frac{k[[Co(C_2O_4)_3]^{3-}][Cu(II)]_{added}}{1 + K_1[S_2O_3^{2-}] + K_1K_2[S_2O_3^{2-}]^2 + [S_4O_6^{2-}]/(K^{1/2}[S_2O_3^{2-}])} \tag{8}$$

When the term $K_1[S_2O_3^{2-}]$ is dominant in the denominator of eqn. (8), eqn. (8) is practically equivalent to the empirical rate law of eqn. (1), and is written as follows.

$$-\frac{d[[Co(C_2O_4)_3]^{3-}}{dt} = \frac{k[[Co(C_2O_4)_3]^{3-}][Cu(II)]_{added}}{K_1[S_2O_3^{2-}]} \tag{8'}$$

Thus, $[Cu(II)]_i$ and k_{obs} in the empirical rate law of eqn. (1) correspond to $[Cu(II)]_{added}$ and k/K_1 in eqn. (8'), respectively.

Determination of Rate Constant

The values of k_{obs} in eqn. (1) were determined to be $(6.3 \pm 0.6) \times 10^{-4}$ s^{-1} in an average of thirty values of V_i obtained at various concentrations of $[S_2O_3^{2-}]_i$, $[Cu(II)]_i$, and $[[Co(C_2O_4)_3]^{3-}]_i$ (see Table I). The rate constant of the reducing reaction of the $[Co(C_2O_4)_3]^{3-}$ ion by the copper(I) ion (*i.e.*, k in eqns. (5) and (8′)) was determined to be $(1.4 \pm 0.1) \times 10^7$ dm^3 mol^{-1} s^{-1} by using the relationship of $k_{obs} = k/K_1$ with $K_1 = 2.24 \times 10^{10}$ dm^3 mol^{-1} [8].

Effect of the Mixing Order of Reactants

When the copper(II) ion concentrations were less than 5×10^{-4} mol dm^{-3}, the induced reducing reaction rate of the $[Co(C_2O_4)_3]^{3-}$ ion was dependent on the mixing order of the reactants. The rate of reaction, which was initiated by mixing the copper(II) solution with a solution containing $S_2O_3^{2-}$ and $[Co(C_2O_4)_3]^{3-}$, was slower than that initiated by mixing the $[Co(C_2O_4)_3]^{3-}$ solution with a solution containing $S_2O_3^{2-}$ and Cu^{2+}. Moreover, the reaction rate increased with increasing the standing time of the reaction solution containing the thiosulfate and copper(II) ions, and the dependence on the standing time was larger at the lower concentrations of the thiosulfate and copper(II) ions. Actually, when concentrations of the thiosulfate and copper(II) ions were large enoguth (e.g., 0.001–0.005 mol dm^{-3} thiosulfate and 0.003 mol dm^{-3} copper(II)), the rate of the reducing reaction of the $[Co(C_2O_4)_3]^{3-}$ ion was independent of the mixing order of the reactants. Consequently, such a dependence of the mixing order of reactants could be attributed to the slowdown of the equilibrium reactions described in eqns. (2)–(4), according to the decreasing concentrations of the thiosulfate and copper(II) ions. Some data on the effect of the mixing order are given in Table II.

Salt Effect on the Reaction Rate

The induced reducing reaction rate of the $[Co(C_2O_4)_3]^{3-}$ ion was hardly influenced by the ionic strengths over the range from 0.005 to 0.1 mol dm^{-3} $NaClO_4$, and was also almost independent of the tetrathionate ion $S_4O_6^{2-}$ as well as the chloride ion Cl^- (see Table III).

TABLE II. Effect of Mixing Order of Reactants[a]

$[S_2O_3^{2-}]_i$ (mol dm^{-3})	10^8 V_i (mol dm^{-3} s^{-1})		
	I	II	III
0.001	3.2	10.0	13.0
0.002	3.6	6.5	7.6
0.003	5.1	5.2	5.7
0.004	4.0	3.9	4.2
0.005	3.4	3.6	3.4

[a] Initial concentrations are 0.003 mol dm^{-3} in $K_3[Co(C_2O_4)_3]$, 1×10^{-4} mol dm^{-3} in $CuSO_4$, and various concentrations in $Na_2S_2O_3$. 25 °C; dark. (I) Reactions were initiated by adding the copper(II) solution into a solution containing the thiosulfate and tris(oxalato)cobaltate(III) ions. (II) Reactions were initiated by adding the $[Co(C_2O_4)_3]^{3-}$ solution into a solution containing the thiosulfate and copper(II) ions, which had stood for a few minutes before the addition. (III) Mixing order is the same as in II, but solutions containing the thiosulfate and copper(II) ions stood for 60 min before mixing them with the $[Co(C_2O_4)_3]^{3-}$ ion.

TABLE III. Salt Effect on the Reaction Rate[a]

Concentration of salts added (mol dm^{-3})	10^7 V_i (mol dm^{-3} s^{-1})	
None	3.8	
0.005 $NaClO_4$	4.5	
0.01 $NaClO_4$	4.5	
0.025 $NaClO_4$	4.5	4.5[b]
0.05 $NaClO_4$	4.9	5.0[b]
0.1 $NaClO_4$	4.9	
0.001 NaCl	3.4	
0.01 NaCl	4.1	4.1[b]
0.1 NaCl	5.1	
0.2 NaCl	5.1	
0.001 $Na_2S_4O_6$	3.7	
0.005 $Na_2S_4O_6$	3.7	
0.01 $Na_2S_4O_6$	3.6	

[a] Conditions as in [a] of Table I. [b] As in [a]; but reactions were initiated by adding the tris(oxalato)cobaltate(III) ion into a solution containing copper(II), thiosulfate, and salts, the solution being left to stand for 30 min before initiating the reaction.

Effect of the Complex-forming Substances

Although the abbreviation EDTA is generally for ethylenediaminetetraacetic acid, *i.e.*, H_4edta, we use, throughout this paper, EDTA for all forms of H_4edta, H_3edta$^-$, H_2edta^{2-}, Hedta^{3-}, and edta^{4-}. When the induced reducing reaction of the $[Co(C_2O_4)_3]^{3-}$ ion was initiated by adding the solution of the thiosulfate and copper(II) ions into a solution containing tris(oxalato)cobaltate(III), and EDTA or oxalate, the rate of the reducing reaction was only a little retarded by the presence of EDTA and was hardly retarded by that of oxalate. On the other hand, when the reaction was initiated by addition of the thiosulfate solution into a solution containing tris(oxalato)cobaltate(III), copper(II), and EDTA or oxalate, the rate of the reducing reaction of $[Co(C_2O_4)_3]^{3-}$ was extremely retarded by EDTA as well as by oxalate (see Table IV). Such a retardation effect also appeared when the reaction was initiated by addition of the copper(II) solution into a solution

TABLE IV. Effect of the Complex-forming Reagents[a]

Concentration of EDTA or oxalate (mol dm^{-3})	10^7 V_i (mol dm^{-3} s^{-1})		
	I	II	III
None	4.0	3.8	3.8
0.001 EDTA	3.4	0.05	
0.005 EDTA	2.9	0.02	0.02
0.010 EDTA	2.4	0.02	
0.001 $Na_2C_2O_4$	3.8	3.0	1.1
0.002 $Na_2C_2O_4$			0.66
0.005 $Na_2C_2O_4$			0.16
0.010 $Na_2C_2O_4$	3.3	0.05	0.06

[a] Conditions except for the coexistence of EDTA or oxalate and for the mixing order of the reactants are the same as those in Fig 1. (I) Reactions were initiated by adding a solution containing the copper(II) and thiosulfate ions into the solution containing $[Co(C_2O_4)_3]^{3-}$ without or with EDTA or oxalate. (II) Reactions were initiated by adding the copper(II) solution into a solution containing $[Co(C_2O_4)_3]^{3-}$ and thiosulfate without or with EDTA or oxalate. (III) Reactions were initiated by adding the thiosulfate solution into a solution containing $[Co(C_2O_4)_3]^{3-}$ and copper(II) without or with EDTA or oxalate.

containing tris(oxalato)cobaltate(III), thiosulfate, and EDTA or oxalate (see Table IV).

Discussion

According to the Marcus theory [5], the rate constant k_{12} of the electron-transfer cross reaction

$$Ox_2 + Red_1 \overset{k_{12}}{\rightleftharpoons} Red_2 + Ox_1 \qquad (9)$$

can be given by eqn. (10) with eqn. (11)

$$k_{12} = (k_{11} k_{22} K_{12} f_{12})^{1/2} \qquad (10)$$

$$\log f_{12} = (\log K_{12})^2 / \{4 \log(k_{11} k_{22} / Z^2)\} \qquad (11)$$

where k_{11} and k_{22} denote the rate constants of the self-exchange electron-transfer reactions for the 1 and 2 species; K_{12} indicates the equilibrium constant of reaction (9); Z is the collision frequency in solution and is usually taken as 10^{11} dm^3 mol^{-1} s^{-1} at 25 °C. When the reaction is of the one-electron transfer reaction, eqn. (10) can be described at 25 °C as follows

$$\log(k_{12}/k_{11}^{1/2}) = \tfrac{1}{2} \log(k_{22} f_{12}) + 8.5\, E^\circ_{12} \qquad (12)$$

where eqns. (10) and (12) can be applied to the outer-sphere reaction under conditions of the negligibly small work terms; the work terms indicate the energies to be required to bring the reactants or products together at the separate distance in the activated complex. The plots $\log(k_{12}/k_{11}^{1/2})$ *versus* E°_{12} are given in Fig. 3 by using the data listed in Table V.

Each plot, except one, is in good agreement with the straight line having a slope of 8.5 which is predicted by eqn. (12). The exception in the case of the reaction between iron(II) and $[Co(C_2O_4)_3]^{3-}$ could be interpreted in that this reaction occurs by the inner-sphere mechanism via carboxyl bridging [3]. The other instances including the reaction between copper(I) and $[Co(C_2O_4)_3]^{3-}$ ions in Fig. 3 and Table V could be of the outer-sphere type in the electron-transfer reactions, and thus, could be eventually described by eqn. (12). The univalent copper(I) ion may result in only a weak electrostatic interaction with the $[Co(C_2O_4)_3]^{3-}$ ion, thus, making carboxyl-bridging with the $[Co(C_2O_4)_3]^{3-}$ ion, in which the three oxalates are rigidly coordinated to the cobalt(III) ion, difficult. Thus, it is probable that the reaction of the copper(I) ion with the $[Co(C_2O_4)_3]^{3-}$ ion accords with eqn. (12) for the outer-sphere mechanism of reaction. Since the intercept of the straight line in Fig. 3 is almost zero, the k_{22} for the self-exchange electron-transfer reaction between $[Co(C_2O_4)_3]^{3-}$ and $[Co(C_2O_4)_3]^{4-}$ should be approximately unity which is the same

TABLE V. Kinetic Data for the Electron-transfer Reactions at 25 °C

Series No.	Reaction system (Ox_2-Red_1)	E°_1 (V)	E°_2 (V)	k_{12} (dm^3 mol^{-1} s^{-1})	k_{11} (dm^3 mol^{-1} s^{-1})
1	$[Co(C_2O_4)_3]^{3-}-Cr^{2+}(aq)$	-0.41^b	0.6^d	$4.0 \times 10^{6\,f}$	$\leqslant 2 \times 10^{-5\,p}$
2	$[Co(C_2O_4)_3]^{3-}-Cu(I)$	0.153^b	0.6^d	$1.4 \times 10^{7\,a}$	$5 \times 10^{7\,h}$ $1.53 \times 10^{8\,i}$
3	$[Co(C_2O_4)_3]^{3-}-Fe(II)$	0.77^b 0.68^n	0.6^d	33^e 23^j 1200^k	0.87 for $Fe^{2+}(aq)^m$ 1010 for $FeOH^{+\,m}$
4	$[Ru(NH_3)_6]^{3+}-Cr^{2+}(aq)$	-0.41^b	0.21^c	$2 \times 10^{2\,c}$	$\leqslant 2 \times 10^{-5\,p}$
5	$[Ru(NH_3)_6]^{3+}-V^{2+}(aq)$	-0.255^b	0.21^c	$7.3 \times 10^{2\,c}$	$1 \times 10^{-2\,g}$
6	$[Ru(NH_3)_6]^{3+}-Cu^{+}(aq)$	0.153^b	0.21^c	$2.2 \times 10^{4\,c}$	$5 \times 10^{7\,h}$ $1.53 \times 10^{8\,i}$

[a] This study. [b] Ref. 9. [c] Ref. 11. [d] Ref. 12. [e] Ref. 2. [f] Ref. 4. [g] Ref. 13. [h] Ref. 14. [i] Ref. 15. [j] Ref. 3. [k] Ref. 1. [m] Ref. 16. [n] Ref. 17. [p] Ref. 18.

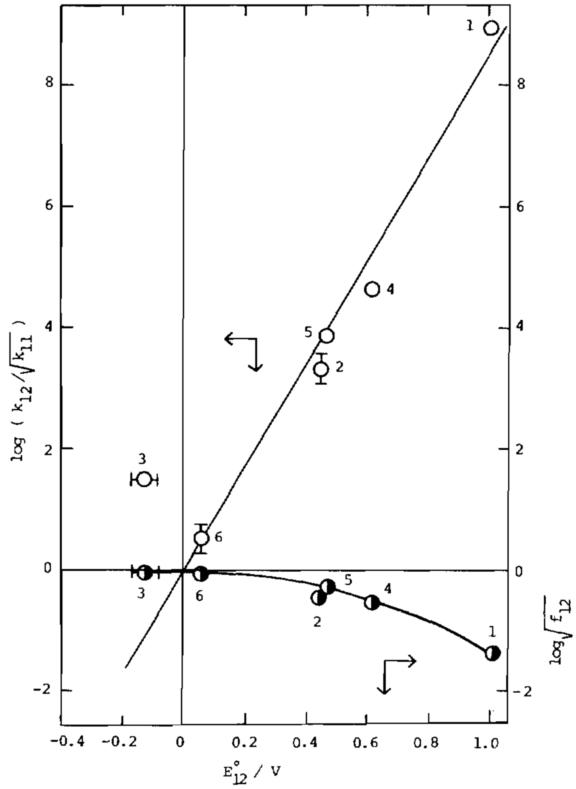

Fig. 3. Plots for eqn. (12) and of $\log f_{12}^{1/2}$ *vs.* E°_{12}. The number alongside each plot indicates the series number in Table V.

magnitude as that for the reaction between $[Ru(NH_3)_6]^{3+}$ and $[Ru(NH_3)_6]^{2+}$. The values of $\log f_{12}^{1/2}$ were calculated by assuming 10^{11} dm^3 mol^{-1} s^{-1} for Z and 1 dm^3 mol^{-1} s^{-1} for k_{22} and were plotted against E°_{12} in Fig. 3 together with plots of $\log(k_{12}/k_{11}^{1/2})$ *versus* E°_{12}. It was found that the changes of f_{12} according to the E°_{12} change did not seriously affect the plots of $\log(k_{12}/k_{11}^{1/2})$ *versus* E°_{12}.

As shown in Table IV, when the reaction is initiated by addition of thiosulfate into a solution containing $[Co(C_2O_4)_3]^{3-}$, copper(II), and EDTA or oxalate, the reducing reaction rate of the $[Co(C_2O_4)_3]^{3-}$ ion is almost completely retarded. Such a strong retardation effect of EDTA and oxalate on the induced reaction rate could be attributed to the decrease of the reduction potential of the copper(II) ion by its complex formation with EDTA or with oxalate. The difference of the standard redox potential between $S_2O_3^{2-}/S_4O_6^{2-}$ and Cu^{2+}/Cu^+ is only 0.07 V [9], and thus the rate of the reducing reaction of the copper(II) ion by the thiosulfate ion, *i.e.* the rate of forward reaction in eqn. (2), could be easily retarded by the complex-forming substances such as EDTA and oxalate.

Although the rate of the reducing reaction of the $[Co(C_2O_4)_3]^{3-}$ ion was not apparently influenced by the molecular oxygen (refer to Fig. 1), the following reactions could not necessarily be denied.

$$Cu^+ + O_2 \rightleftharpoons O_2^- + Cu^{2+} \qquad (13)$$

$$[Co(C_2O_4)_3]^{3-} + O_2^- \longrightarrow Co^{2+} + 3C_2O_4^{2-} + O_2 \qquad (14)$$

If the rate of reaction (14) is as fast as that of reaction (5), the oxygen effect could practically not be observed. Recently, the present authors [10] have reported the rate constant of reaction (14) to be 6 X 10^8 dm^3 mol^{-1} s^{-1} which is some tenfold larger than 1.4 X 10^7 dm^3 mol^{-1} s^{-1} of reaction (5). The latter value was evaluated by the kinetic study in the present paper. Since both reactions (13) and (14) are very likely to occur, these reactions would occur simultaneously with reactions (2)–(5) in the presence of oxygen.

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