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Oxidation of Chromium(II) Complexes. I. Kinetics of the Oxidation of Tris(2,2′-bipyridine)- and of Tris(1,10-phenanthroline)chromium(II) Complexes with Hexaamminecobalt(III) Ion[1]

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Kinetic studies have been carried out on the oxidation of $[Cr(bipy)_3]^{2+}$ and $[Cr(phen)_3]^{2+}$ with $[Co(NH_3)_6]^{3+}$ (bipy and phen denote 2,2′-bipyridine and 1,10-phenanthroline, respectively). The rate law is found to be $-d[Cr(II)]/dt = k_1[Co(III)][Cr(II)] + k_2[Cr(II)]$. Simulation procedures with an analogue computer were applied for the analysis of these reactions. The rate constant k_1 (direct oxidation) and k_2 (dissociation) for $[Cr(bipy)_3]^{2+}$ were 180 $M^{-1} s^{-1}$ and 0.120 s^{-1} ($\mu=0.11$ with NaCl, at 25 °C) and those for $[Cr(phen)_3]^{2+}$ were 310 $M^{-1} s^{-1}$ and 0.630 s^{-1} ($\mu=0.20$ with NaCl, at 25 °C), respectively. The larger value of k_1 for $[Cr(phen)_3]^{2+}$ as compared with that of k_1 for $[Cr(bipy)_3]^{2+}$ was interpreted as being due to the good electron conductivity of the phenanthroline as a ligand in the activated state. The activation parameters were obtained as follows: in the case of $[Cr(bipy)_3]^{2+}$, $\Delta H^{\ne}=7.5$ kcal/mol and $\Delta S^{\ne}=-23$ e.u. for the k_1 path, and $\Delta H^{\ne}=17.2$ kcal/mol and $\Delta S^{\ne}=-5$ e.u. for the k_2 path; and in the case of $[Cr(phen)_3]^{2+}$, $\Delta H^{\ne}=8.2$ kcal/mol and $\Delta S^{\ne}=-20$ e.u. for the k_1 path, and $\Delta H^{\ne}=21.2$ kcal/mol and $\Delta S^{\ne}=+12$ e.u. for the k_2 path.

Many investigators[2-7] have pointed out that the oxidation reaction of $[Cr(bipy)_3]^{2+}$ with $[Co(NH_3)_6]^{3+}$ proceeds *via* an outer-sphere mechanism. Zwickel and Taube[6] reported on the rate constants under various conditions, and deduced from the ion-exchange of the product that there is no possibility of the formation of ligand-deficient species ($[Cr(H_2O)_2(bipy)_2]^{3+}$ or $[Cr(OH)_2(bipy)_2]^{+}$) in the course of the reaction. Murray and Waind[8] and Baker and Mehta[9] demonstrated, by spectrophotometric means in the case of the former and by polarographic means in the case of the latter, that $[Cr(H_2O)_2(bipy)_2]^{3+}$ is produced in the oxidation of $[Cr(bipy)_3]^{2+}$ with $[Co(NH_3)_6]^{3+}$. Endicott and Taube,[5] although their argument is not in line with that of Zwickel and Taube,[6] suggested that $[Cr(bipy)_3]^{2+}$ is very substitution-labile and the possibility exists that one of the coordination positions is exposed by opening one of the chelate rings in the activated state. The formation of $[Cr(H_2O)_2(bipy)_2]^{3+}$ and of $[Cr(OH)_2(bipy)_2]^{+}$ is not explained by the aquation of $[Cr(bipy)_3]^{3+}$ produced by oxidation, because Cr(III) complex is substitution-inert. This must be elucidated by a dissociative mechanism for $[Cr(bipy)_3]^{2+}$ into $[Cr(H_2O)_2(bipy)_2]^{2+}$, $[Cr(OH)(H_2O)(bipy_2)]^{+}$, or $[Cr(OH)_2(bipy)_2]$.

The present investigation was carried out following the kinetic work of Zwickel and Taube[6] by means of a stopped-flow technique, the rate equations being analyzed by simulation procedures with an analogue computer. The investigation also aims at a comparison of the kinetic parameters of $[Cr(bipy)_3]^{2+}$ with those of $[Cr(phen)_3]^{2+}$, which is similar to $[Cr(bipy)_3]^{2+}$ in structure.

Experimental

Reagents. Hexaamminecobalt(III) chloride monohydrate prepared by the usual method was purified several times. Hydrochloric acid was purified by distillation. The purity of 2,2′-bipyridine and 1,10-phenanthroline was examined by measuring the infrared spectra by KBr disk method. All other chemicals were of guaranteed grade and were not purified further.

Preparation of the Reactant Solutions. Solutions of $[Co(NH_3)_6]^{3+}$ were prepared by dissolving a weighed sample of $[Co(NH_3)_6]Cl_3 \cdot H_2O$ in NaCl solution containing a given amount of 2,2′-bipyridine. Solutions of $[Cr(bipy)_3]^{2+}$ were prepared as follows: Cr metal (99.99%, Johnson Matthey) was dissolved in HCl which had been deaerated with a vacuum apparatus. After the excess HCl had been removed by distilling under reduced pressure, the residue was dissolved in NaCl solution containing a given amount of 2,2′-bipyridine. Solutions of $[Cr(phen)_3]^{2+}$ were prepared by the same procedure except that 1,10-phenanthroline was used instead of 2,2′-bipyridine. All the solutions were deaerated three times with a vacuum apparatus.

Measurements of Changes in the Absorbance. The stopped-flow apparatus used for following the reactions was a Yanaco SPS-1 spectrophotometer connected with an Iwasaki MS-5019A synchroscope with a memory device. The spectrophotometer used for measuring the absorption curves was a

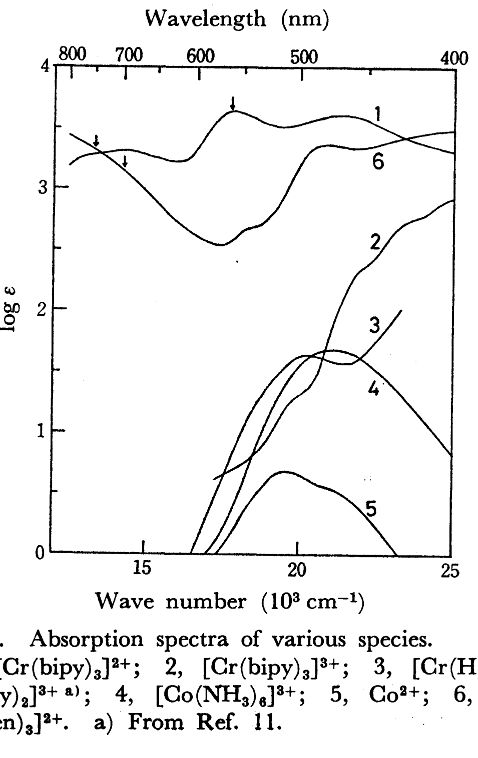

Fig. 1. Absorption spectra of various species.
1, $[Cr(bipy)_3]^{2+}$; 2, $[Cr(bipy)_3]^{3+}$; 3, $[Cr(H_2O)_2(bipy)_2]^{3+}$ [a]; 4, $[Co(NH_3)_6]^{3+}$; 5, Co^{2+}; 6, $[Cr(phen)_3]^{2+}$. a) From Ref. 11.

Hitachi 124 spectrophotometer. Introduction of the reactant solutions into the stopped-flow apparatus and the technique of the kinetic measurements followed the same procedures as the usual stopped-flow methods. Measurements of the absorption spectra of $[Cr(bipy)_3]^{2+}$ and $[Cr(phen)_3]^{2+}$ complexes were made by sealing the solution in a 10-mm quartz cell in the absence of air. The spectra are shown in Fig. 1 along with those of the other complexes concerned. The absorption spectra of $[Cr(bipy)_3]^{2+}$ and $[Cr(phen)_3]^{2+}$ complexes are in line with those reported,[10] except for slight differences in intensity.

Changes in the transmittance as a function of time were followed with the stopped-flow apparatus in an excess of $[Co(NH_3)_6]^{3+}$ at 562.5 nm ($\varepsilon=4340\ \mathrm{l\cdot mol^{-1}\ cm^{-1}}$) for $[Cr(bipy)_3]^{2+}$ and at either 700 nm ($\varepsilon=1397$) or 750 nm ($\varepsilon=2046$) for $[Cr(phen)_3]^{2+}$. At each wavelength where the reaction was followed, the molar extinction coefficient of each reductant was *ca.* 500 times that of any other species present (Fig. 1). Oscilloscope trace of transmittance as a function of time is shown in Fig. 2. The gradual increase in transmittance with time (curve 2) corresponding to the disappearance of $[Cr(bipy)_3]^{2+}$ at a given wavelength was observed after the flow of the solution stopped (point A, curve 1). Curve 2 was converted into one showing the change in absorbance or concentration of Cr(II) complex *vs.* time using the molar extinction coefficient (ε), the value of % transmittance (T_∞) at 'infinite' time (curve 3), and the value of 5% calibration signal corresponding to $T_\infty\times0.05$ (curve 4). T_∞ was found to be 99.38% for the final solution in the kinetic run. The stopped-flow measurements were repeated several times for the same solution, and were repeated for $[Cr(phen)_3]^{2+}$ as well as for $[Cr(bipy)_3]^{2+}$ under various temperatures, oxidant concentrations and hydrogen ion concentrations.

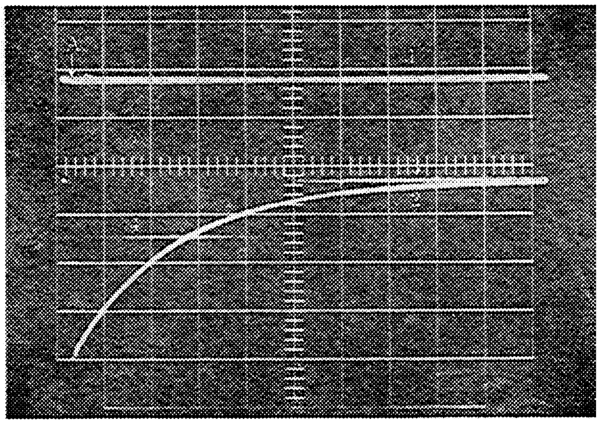

Fig. 2. Oscilloscope trace of transmittance (at 562.5 nm) of $[Cr(bipy)_3]^{2+}$ system as a function of time; $[Cr(bipy)_3{}^{2+}]=2.68\times10^{-4}$ M, $[Co(NH_3)_6{}^{3+}]=2.49\times10^{-3}$ M, $[bipy]=1.0\times10^{-2}$ M, pH=5.32, $\mu=0.10$ with NaCl, at 25.1 °C.
Curve 1, flow signal; 2, reaction signal; 3, transmittance (T_∞) at "infinite" time (99.38%); 4, 5% calibration signal. The abscissa scale is 1 sec per major division and the ordinate scale is in arbitrary unit of transmittance.

No attempt was made to identify the products of reaction or confirm directly the stoichiometry, which was assumed in each case to be $Cr(II)+Co(III)\rightarrow Cr(III)+Co(II)$ on the basis of the earlier observations of these and related reactions.

pH Measurements. The pH of the oxidant solution was measured with a pH meter. As it was impossible to measure directly the value of pH of the reductant solution, the value was estimated by measuring the pH of the solution in which Cr^{2+} ion was absent, because it was assumed that addition of Cr^{2+} ion to the solution does not affect the pH value under the experimental conditions of the present work, taking the acidity constants[12] of the bipyridinium and phenanthrolinium ions into consideration. The pH of the mixture of the reactant solutions was assumed to lie between the two pH's of the two reactant solutions, the values of which were within 0.1 pH unit of the average.

Analysis of Data

Analogue Computer Assembly. The analogue computer for analyzing the rate equations has circuits as shown in Figs. 3(a),[13] 3(b), and 4.

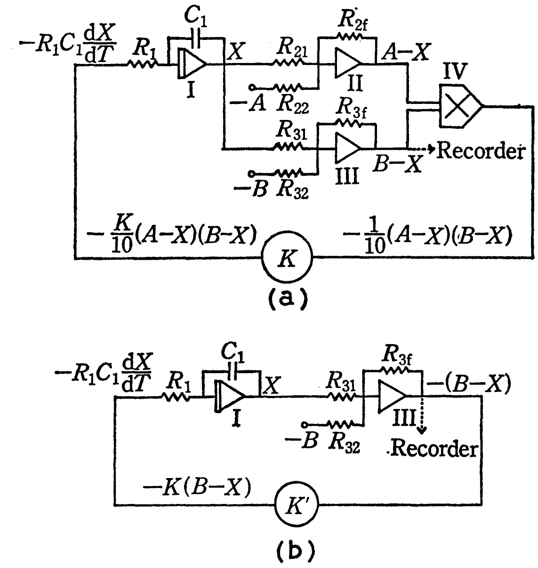

Fig. 3. Analogue computer circuit diagrams; (a) for the second-order reaction, and (b) for the first-order reaction, where inverter being omitted.
$C_1=10\ \mu F$; $R_1=100\ k\Omega$; $R_{21}=R_{22}=R_{2f}=R_{31}=R_{32}=10\ k\Omega$; $R_{3f}=10\ k\Omega$ or $100\ k\Omega$; $K=K'=1\ k\Omega$. I, SA-3a; II and III, SQ-10a; IV, Quarter-square multiplier, Model 4030/25.

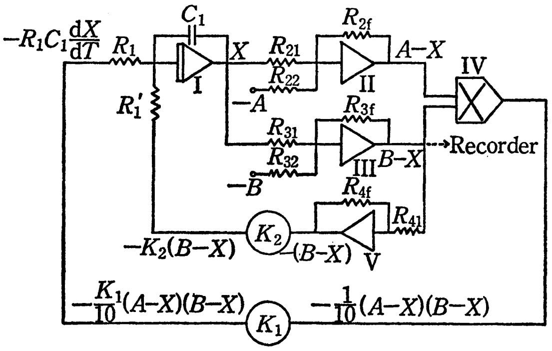

Fig. 4. Analogue computer circuit diagram for the composite first- and second-order reactions.
$C_1=10\ \mu F$; $R_1=R_1'=100\ k\Omega$; $R_{21}=R_{22}=R_{2f}=R_{31}=R_{32}=R_{41}=R_{4f}=10\ k\Omega$; $R_{3f}=10\ k\Omega$ or $100\ k\Omega$; $K_1=K_2=1\ k\Omega$.
I, SA-3a; II and III, SQ-10a; IV, Quarter-square multiplier, Model 4030/25; V, SA-3a.

Operational amplifiers and a function multiplier were supplied by Philbrick–Nexus and Burr-Brown, respectively. A voltage regulator Type VK 15012W, Volgen, was used as the D.C. power stabilizer. In the figures, I, II, III, and V are operational amplifiers; I integrator, II and III adder, and V inverter. Function multiplier IV was used for multiplying two variables, and attenuators K, K', K_1, and K_2 were used for multiplying a constant value. For the resistor R_{3f}, a value of either 10 kΩ or 100 kΩ was used, depending on the magnitude of the input signal of III. The analogue computer with the circuit shown in Fig. 4 was used for the first time for simulating the composite first- and second-order reactions. The voltage change corresponding to the change in the concentration of the chromium(II) complex was followed by the output signal of III as a function of time and was recorded with an EPR-2TC Toa Electronics recorder. The exact values of the individual components were determined prior to use and applied as corrections in the final evaluation of the rate constants measured by the analogue computer simulations.

Simulation Procedures for Measuring Rate Constants. For determining the rate constants graphically by using the change in a concentration as a function of time, the initial concentration of each of the reactants and the concentration at each instantaneous time after the reaction starts should be known. In the present investigation, however, it is supposed that Cr(II) complex was oxidized partially before the reactant solutions were mixed, owing to its sensitiveness to oxidation, that the reactant solutions were not mixed instantaneously because of the so-called dead-time resulting from the mechanical restriction of the stopped-flow apparatus, and that both reactants are consumed during the time in which reactants go from the mixing point to the cell through which a light beam for the observation passes. For these reasons, the rate constants cannot be determined exactly by a graphical method. Thus the simulation method with an analogue computer was attempted for analyzing the reaction. The simulation for the second-order reaction, assumed to be $\mathrm{Cr(II)+Co(III)\rightarrow Cr(III)+Co(II)}$, was carried out according to Nakanishi's method,[13] *viz.*, with an analogue computer (Fig. 3(a)); the voltage, $-B$, corresponding to the effective initial concentration (calculated from the absorbance at the starting point of the curve of the absorbance change and the molar extinction coefficient) of Cr(II) complex was applied to the adder III as the input signal, and the circuit was closed at the machine time $T=0$. The output voltage of III was then followed as a function of time T, and the voltage change with time was recorded on the recorder. Thus, if the curve obtained by the simulation procedure was fitted to the curve of the change in concentration with time by adjusting the input voltage ($-A$) of adder II and the dial reading of the helipot K, $-A$ could be considered to correspond to the effective initial concentration of Co(III) complex and the reading of K to a value proportional to the rate constant. Thus, by comparing the assumed rate equation (1) or (1′) with machine equation (2), equation (3) is obtained as follows:

$$-\frac{\mathrm{d[Cr(II)]}}{\mathrm{d}t} = k_{\mathrm{obs}}\mathrm{[Co(III)][Cr(II)]} \tag{1}$$

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k_{\mathrm{obs}}(a-x)(b-x) \tag{1'}$$

$$\frac{\mathrm{d}X}{\mathrm{d}T} = \frac{K}{10R_1C_1}(A-X)(B-X) \tag{2}$$

$$k_{\mathrm{obs}} = \frac{\alpha\beta K}{10R_1C_1} \tag{3}$$

where k_{obs} is an apparent rate constant obtained by analyzing the rate equation as a second-order reaction; a and b are effective initial concentrations of Co(III) and Cr(II) complexes, respectively; x is the amount of reactant consumed at an effective time t after the reaction signal became observable; X is the voltage on C_1 at time T after the circuit is switched on and is proportional to x; α is a factor in $\mathrm{V\cdot l\cdot mol^{-1}}$ to convert the voltage $(B-X)$ into the concentration $(b-x)$; β is a dimensionless factor to convert the machine time T into the reaction time t; and $1/R_1C_1$ is a correction factor whose reciprocal is a time constant of the integrator I. Examples of the simulation actually performed are shown (Fig. 5(a) and (b), curve 1).

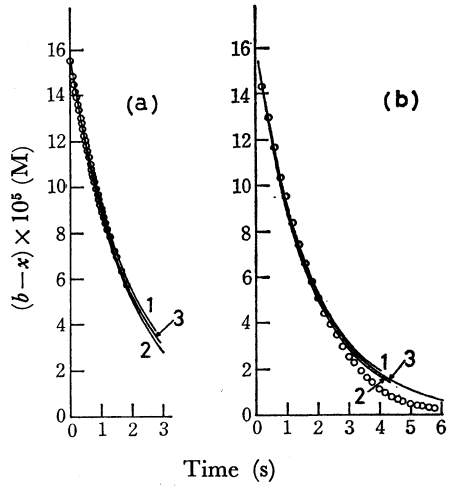

Fig. 5. Typical examples of analogue computer simulations for the oxidation of $[Cr(bipy)_3]^{2+}$ with $[Co(NH_3)_6]^{3+}$.
The open-circled points in (a) and (b) refer to No. 2—4 and No. 2—2 in Table 1, respectively. Solid curves 1, 2, and 3 are those obtained by the simulations for the second-order reaction (Eq. (1)) with the circuit of Fig. 3(a), the first-order reaction (Eq. (5)) with that of Fig. 3(b), and the composite first- and second-order reaction (Eq. (9)) with that of Fig. 4, respectively.

However, the values of k_{obs} thus obtained at the same temperature decrease as $[Co(NH_3)_6]^{3+}$ concentration increases (Tables 1 and 2). The results obtained by the graphical method are also shown.

It was assumed that k_{obs} is expressed by the sum of the term independent of [Co(III)] and the term reciprocally proportional to it:

$$k_{\mathrm{obs}} = k_1 + \frac{k_2}{\mathrm{[Co(III)]}} \tag{4}$$

TABLE 1. APPARENT SECOND-ORDER RATE CONSTANTS FOR $[Cr(bipy)_3]^{2+}$ SYSTEMS$^{a)}$

Run No.$^{b)}$	$[Cr(bipy)_3{}^{2+}]$ (mM)$^{c)}$	$[Co(NH_3)_6{}^{3+}]$ (mM)$^{c)}$	Temp (°C)	k_{obs} ($M^{-1}s^{-1}$) (graphical)	(simulation)
1— 3	0.252	0.275	25.4	1980	1890
1— 4	0.252	0.275	25.4	—$^{d)}$	1930
1— 5	0.252	0.275	25.4	2280	1910
2—21	0.249	2.52	39.9	524	547
2—25	0.249	2.52	39.9	543	561
2—30	0.249	2.52	34.8	450	414
2—31	0.249	2.52	34.8	436	413
2—16	0.249	2.52	29.9	295	311
2—17	0.249	2.52	29.9	301	314
2— 2	0.249	2.52	25.1	253	226
2— 4	0.249	2.52	25.1	247	225
2— 8	0·249	2.52	20.3	204	172
2—12	0.249	2.52	20.1	174	173
3— 1	0.268	2.49	34.6	511	410
3—12	0.268	2.49	25.1	219	233
3— 8	0.268	2.49	16.1	144	130

a) At 562.5 nm. b) No. 1-series; pH=6.32, μ=0.11(NaCl): 2-series; pH=6.30, μ=0.11(NaCl): 3-series; pH =5.32, μ=0.10(NaCl). c) Each reactant solution contains 0.010 M 2,2′-bipyridine. d) Graphical analysis not carried out.

TABLE 2. APPARENT SECOND-ORDER RATE CONSTANTS FOR $[Cr(phen)_3]^{2+}$ SYSTEMS$^{a)}$

Run No.	$[Cr(phen)_3{}^{2+}]$ (mM)$^{b)}$	$[Co(NH_3)_6{}^{3+}]$ (mM)$^{b)}$	Temp (°C)	k_{obs} ($M^{-1}s^{-1}$) (graphical)	(simulation)
28— 7	1.24	2.50	24.8	763	762
27—14$^{c)}$	1.27	4.98	25.1	522	520
27—15	1.27	4.98	25.1	512	514
29—33	1.12	9.99	39.8	1060	1010
29—28	1.12	9.99	35.1	813	786
29—17	1.12	9.99	30.0	540	530
29— 5	1.12	9.99	25.1	434	372
29— 8	1.12	9.99	25.1	371	373
29—11	1.12	9.99	20.0	326	263
29— 9	1.12	9.99	19.7	303	268

a) pH=6.05±0.10, μ=0.20(NaCl), λ=750 nm except No. 27—14. b) Each reactant solution contains 0.012 M 1,10-phenanthroline. c) λ=700 nm.

The rate constants k_1 and k_2 should be obtained from the intercept and the slope, respectively, by plotting k_{obs} against $[Co(III)]^{-1}$ (Fig. 6, lines 1 and 2). The results for $[Cr(bipy)_3]^{2+}$ and $[Cr(phen)_3]^{2+}$ complexes are given in Table 4.

The reaction was analyzed by assuming that it is of first-order:

$$-\frac{d[Cr(II)]}{dt} = k'_{obs}[Cr(II)] \tag{5}$$

For circuit diagram, see Fig. 3(b). The simulation procedure was almost the same as in the case of the second-order reaction. Examples are shown by curve 2 in Fig. 5(a) and (b). In this case, the machine equation is expressed as follows:

$$\frac{dX}{dT} = \frac{K'}{R_1C_1}(B-X) \tag{6}$$

If the dial of the helipot K' is properly adjusted, this turns out to correspond to Eq. (5), and we have

$$k'_{obs} = \frac{\beta K'}{R_1C_1} \tag{7}$$

The values of k'_{obs} thus obtained increase with the increase in concentration of $[Co(NH_3)_6]^{3+}$ at the same temperature (Table 3). Thus, it was assumed that k'_{obs} contains a term proportional to the concentration of Co(III):

$$k'_{obs} = k_1[Co(III)] + k_2 \tag{8}$$

The values of k_1 and k_2 obtained are given in Table 4.

Both equations obtained by substituting Eq. (4) into Eq. (1) and Eq. (8) into Eq. (5), respectively, become the same as the following equation:

$$-\frac{d[Cr(II)]}{dt} = k_1[Co(III)][Cr(II)] + k_2[Cr(II)] \tag{9}$$

However, the rate constants k_1 and k_2 obtained from

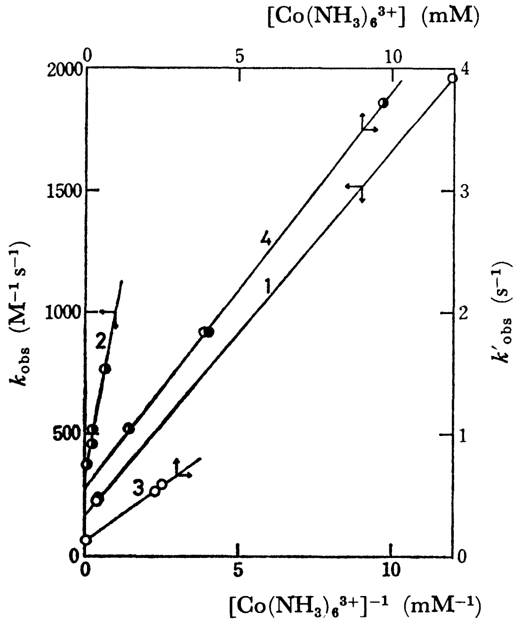

Fig. 6. Relationships of k_{obs} and k'_{obs} at 25 °C to $[Co(NH_3)_6{}^{3+}]^{-1}$ and $[Co(NH_3)_6{}^{3+}]$, respectively.[a] Data are taken from Tables 1, 2, and 3. ○, $[Cr(bipy)_3]^{2+}$; ◑, $[Cr(phen)_3]^{2+}$.

a) The concentration of $[Co(NH_3)_6]^{3+}$ ion was evaluated by using voltages $-A$ and $-B$ for $[Co(NH_3)_6]^{3+}$ ion and Cr(II) complex, respectively, and the concentration of Cr(II) complex at the starting poing of the simulation (T=0) according to the equation, $[Co(III)]_{T=0}=(A/B)[Cr(II)]_{T=0}$.

TABLE 3. APPARENT FIRST-ORDER RATE CONSTANTS AT 25 °C FOR $[Cr(bipy)_3]^{2+}$ AND $[Cr(phen)_3]^{2+}$ BY SIMULATION

Reductant	Run No.[a]	$[Co(NH_3)_6{}^{3+}]$ (mM)	k'_{obs} (s^{-1})
$[Cr(bipy)_3]^{2+}$	1— 5	0.275	0.115±0.003
	3—12	2.49	0.508±0.010
	2— 2	2.52	0.590±0.010
	2— 4	2.52	0.576±0.005
$[Cr(phen)_3]^{2+}$	28— 7	2.50	1.03
	27— 8[b]	4.98	1.84
	27—15	4.98	1.84
	29— 5	9.99	3.72

a) The numerals are the same as those given in the first columns of Tables 1 and 2. b) The conditions are the same as those of No. 27—15.

k_{obs} according to Eq. (4) do not agree with those obtained from k'_{obs} according to Eq. (8) (Table 4). This discrepancy is caused by the fact that concentrations of Co(III) (abscissa, Fig. 6) change during the course of the reaction. (The effective initial concentrations of Co(III) are plotted in Fig. 6). Thus, in order to obtain k_1 and k_2 accurately, it is necessary to simulate Eq. (9) directly. For this purpose, a simulator (Fig. 4) was constructed.

The machine equation for the simulator is expressed as follows:

TABLE 4. FIRST- AND SECOND-ORDER RATE CONSTANTS[a]

	Rate constant[b]	Reductant	
		$[Cr(bipy)_3]^{2+}$	$[Cr(phen)_3]^{2+}$
From k_{obs} and Fig. 6 (lines 1 and 2)	k_1	165±8	300±10
	k_2	0.15±0.01	0.69±0.04
From k'_{obs} and Fig. 6 (lines 3 and 4)	k_1	200±10	321±10
	k_2	0.10±0.01	0.57±0.03
Averaged value	k_1	183±18	311±11
	k_2	0.12_5±0.02_5	0.63±0.06
From simulations for Eq. (9)[c]	k_1	180±3	310±6
	k_2	0.120±0.002	0.630±0.010

a) Data of k_{obs} and k'_{obs} at 25 °C for $[Cr(bipy)_3]^{2+}$ and $[Cr(phen)_3]^{2+}$ were taken from Tables 1, 2, and 3. b) k_1 in $M^{-1}s^{-1}$ and k_2 in s^{-1}. c) Taken with the analogue computer whose circuit is shown in Fig. 4.

$$\frac{dX}{dT}=\frac{K_1}{10R_1C_1}(A-X)(B-X)+\frac{K_2}{R_1C_1}(B-X) \qquad (10)$$

where K_1 and K_2 are proportional to k_1 and k_2, respectively, and given by

$$k_1=\frac{\alpha\beta K_1}{10R_1C_1} \qquad (11)$$

$$k_2=\frac{\beta K_2}{R_1C_1} \qquad (12)$$

The examples of the simulation carried out with this circuit are shown by curve 3 in Fig. 5(a) and (b). The values* of k_1 and k_2 thus obtained under the various conditions were constant irrespective of the concentration of Co(III) at a given temperature as shown in Table 5.

The accuracy of each rate constant obtained by the above procedures was within *ca.* 2% in relative error (Tables 1, 2, 3, and 5).

Therefore, k_1 and k_2 are considered to be the rate constants for the second-order and the first-order reactions, respectively, and it is concluded that Eq. (9) is adequate as the rate law for the present systems.

Results and Discussion

It was found that satisfactory values of rate constants in the oxidation reaction of $[Cr(bipy)_3]^{2+}$ and of $[Cr(phen)_3]^{2+}$ complexes with $[Co(NH_3)_6]^{3+}$ complex (Tables 1 and 2) cannot be obtained by the usual graphical method of analysis. However, by means of simulation procedures with an analogue computer (Fig. 3(a) and (b)), the apparent rate constants of appropriate values could be obtained for the second-order and the first-order reactions (Tables 1, 2, and 3). Both curves 1 and 2 obtained by these simulations deviate from the observed points in the later stage of the reaction (Fig.

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* The values of k_{obs} and k'_{obs}, obtained with the circuits for simulations of the second-order and first-order reactions, respectively, do not correspond to those of k_1 and k_2 obtained by simulating as the composite reaction, and differ significantly. The values of k_{obs} and k'_{obs} are dependent on and those of k_1 and k_2 independent of the concentration of Co(III) complex.

TABLE 5. RATE CONSTANTS k_1 AND k_2 FOR $[Cr(bipy)_3]^{2+}$ AND $[Cr(phen)_3]^{2+}$ BY SIMULATION PROCEDURES[a]

Reductant	Run No.[b]	Temp (°C)	k_1 ($M^{-1}s^{-1}$)	k_2 (s^{-1})
$[Cr(bipy)_3]^{2+}$	1—5	25.4	180	0.120
	2—2	25.1	180	0.120
	2—4	25.1	180	0.120
	2—21	39.9	340	0.480
	2—25	39.9	347	0.492
	2—8	20.3	146	0.0722
	2—12	20.1	144	0.0707
$[Cr(phen)_3]^{2+}$	28—6[c]	24.8	306	0.630
	28—7	24.8	312	0.627
	27—8	25.1	310	0.630
	27—14	25.1	310	0.630
	27—15	25.1	311	0.630
	29—5	25.1	310	0.630
	29—6[d]	25.1	310	0.630
	29—8	25.1	310	0.630
	29—30[e]	39.9	636	3.69
	29—33	39.8	636	3.69
	29—34[e]	39.8	615	3.69
	29—9	19.7	241	0.338
	29—11	20.0	241	0.338

a) Simulations were carried out by means of Eq. (9). b) The numerals are the same as those given in Tables 1, 2, and 3 unless otherwise stated. c) Conditions the same as those of No. 28—7. d) Conditions the same as those of No. 29—5. e) Solution compositions the same as those of No. 29—33.

5(b)). This discrepancy might be mainly due to the formation of $[Cr(OH)_2(bipy)_2]^+$, since the value of pH increased to *ca.* 8.5 in the final solution of the reaction. This is supported by the fact that the absorption spectrum of the reaction product[8] coincides with $[Cr(OH)_2(bipy)_2]^+$,[11] and it changes to $[Cr(H_2O)_2(bipy)_2]^{3+}$[11] on acidification.[8] The value of T_∞ is calculated to be 99.38%, which is just the same as the observed value (Fig. 2), if we assume that *ca.* 81% of the Cr(III) products is $[Cr(OH)_2(bipy)_2]^+$ ($\varepsilon_{562.5nm}=35\ l\cdot mol^{-1}\ cm^{-1}$)[11] and the rest is $[Cr(bipy)_3]^{3+}$, whereas the value is obtained to be 99.66% if we assume the formation of $[Cr(H_2O)_2(bipy)^2]^{3+}$ instead of $[Cr(OH)_2(bipy)_2]^+$. Thus, the product present as a ligand-deficient species is considered to be either $[Cr(H_2O)_2(bipy)_2]^{3+}$ or $[Cr(OH)_2(bipy)_2]^+$. The formation of the ligand-deficient species is explained by either an acid hydrolysis or a base hydrolysis. The dissociation of $[Cr(bipy)_3]^{2+}$ *via* the base hydrolysis becomes predominant with increase in pH of the solution in the later stage of the reaction, although the base hydrolysis does not occur in the earlier stage of the reaction because of the acidity. Since the dissociation rate for the base hydrolysis is considered to be greater than that for the acid hydrolysis,[14] the consumption of $[Cr(bipy)_3]^{2+}$ becomes more marked in the later stage than in the earlier stage of the reaction. The deviation of the simulation curve from the observed plot in the later stage of the reaction (Fig. 5(b)) can thus be explained. The curve-fitting procedures were applied during the time in which 65—70% of the effective initial concentration of each Cr(II) complex undergoes change by the reaction. The values of the rate constants thus obtained would not be affected by the base hydrolysis.

The results obtained for the rate constants for the oxidation and dissociation of $[Cr(bipy)_3]^{2+}$ and $[Cr(phen)_3]^{2+}$ complexes are shown in Table 5. The excellent constancy of the rate constants obtained under a wide variety of $[Cr(NH_3)_6]^{3+}$ concentrations validates the assumed rate law (Eq. (9)). Since the reaction involves the processes of both second-order (k_1 path) and first-order (k_2 path), it seems that the reaction of $[Cr(bipy)_3]^{2+}$ with $[Co(NH_3)_6]^{3+}$ proceeds *via* the composite processes of the direct oxidation of the former with the latter (second-order) and the dissociation of the former into $[Cr(H_2O)_2(bipy)_2]^{2+}$ (first-order). Provided the oxidation of $[Cr(H_2O)_2(bipy)_2]^{2+}$ is more rapid than the dissociation of $[Cr(bipy)_3]^{2+}$ and the concentration of the former is very low, the dissociation process of $[Cr(bipy)_3]^{2+}$ becomes the rate-determining step for the oxidation of the dissociated species, and it follows that the rate of oxidation of $[Cr(H_2O)_2(bipy)_2]^{2+}$ with $[Co(NH_3)_6]^{3+}$ is first-order in $[Cr(bipy)_3]^{2+}$ and zero-order in $[Co(NH_3)_6]^{3+}$. Consequently, the most probable mechanisms of these reactions can be expressed as follows:

$$[Cr(bipy)_3]^{2+} + [Co(NH_3)_6]^{3+} \xrightarrow{k_1} [Cr(bipy)_3]^{3+} + Co^{2+} + 6NH_3 \tag{13}$$

$$[Cr(bipy)_3]^{2+} + 2H_2O \underset{k_3}{\overset{k_2}{\rightleftharpoons}} [Cr(H_2O)_2(bipy)_2]^{2+} + bipy \tag{14}$$

$$[Cr(H_2O)_2(bipy)_2]^{2+} + [Co(NH_3)_6]^{3+} \xrightarrow{k_4} [Cr(H_2O)_2(bipy)_2]^{3+} + Co^{2+} + 6NH_3 \tag{15}$$

Baker and Mehta[9] assumed the rate constant k_5 of the equation

$$[Cr(H_2O)_2(bipy)_2]^{2+} + [Cr(bipy)_3]^{3+} \underset{k_6}{\overset{k_5}{\rightleftharpoons}} [Cr(H_2O)_2(bipy)_2]^{3+} + [Cr(bipy)_3]^{2+} \tag{16}$$

to be of the order of $10^5\ M^{-1}\ s^{-1}$. Since both oxidants in the reactions of Eqs. (15) and (16) are the 'outer-sphere' type of complex and the reductant $[Cr(H_2O)_2(bipy)_2]^{2+}$ is the low-spin[8] type of complex, it is assumed that k_4 and k_5 are at least of the same order of magnitude. Further, the rate constant k_3 is assumed to be *ca.* $10^3\ M^{-1}\ s^{-1}$ from equilibrium[15] and kinetic[7,9] data. Thus it is estimated that the rates of Eqs. (14) and (15) satisfy the relations

$$k_3[bipy] < k_4[Co(NH_3)_6{}^{3+}] \tag{17}$$

$$k_2[Cr(bipy)_3{}^{2+}] < k_4[Cr(H_2O)_2(bipy)_2{}^{2+}][Co(NH_3)_6{}^{3+}] \tag{18}$$

under the present experimental conditions. Thus the forward reaction of Eq. (14) is concluded to be the rate-determining step for the oxidation of the dissociated complex with $[Co(NH_3)_6]^{3+}$. The following should be taken into account in Eqs. (13), (14), and

(15): the effect of $[Cr(bipy)_3]^{3+}$ formed by the reaction of Eq. (13) on the oxidation of $[Cr(H_2O)_2(bipy)_2]^{2+}$ (k_5 path), and the effect of $[Cr(H_2O)_2(bipy)_2]^{3+}$ formed by the reaction of Eq. (15) on the oxidation of $[Cr(bipy)_3]^{2+}$ (k_6 path).

If the reaction of the k_5 path affects reaction (15), these reactions are regarded as competition reactions for the oxidation of $[Cr(H_2O)_2(bipy)_2]^{2+}$. Since $[Cr(bipy)_3]^{2+}$ is produced by the reaction of the k_5 path, the value of the rate constant k_2 becomes smaller with the decrease in the concentration of $[Co(NH_3)_6]^{3+}$. However, the results in Table 5 show a constancy of the rate constant k_2 in a wide range of $[Co(NH_3)_6]^{3+}$ concentrations, indicating that the effect of $[Cr(bipy)_3]^{3+}$ (k_5 path) on the dissociation (k_2 path) is negligible. This is explained by the relation

$$k_5[Cr(bipy)_3{}^{3+}] \ll k_4[Co(NH_3)_6{}^{3+}] \qquad (19)$$

This holds in a large excess of $[Co(NH_3)_6]^{3+}$ as compared with $[Cr(bipy)_3]^{2+}$, since the relation $[Cr(bipy_3)^{3+}] \ll [Co(NH_3)_6{}^{3+}]$ also holds if we consider the formation of $[Cr(bipy)_3]^{3+}$ by the direct oxidation of $[Cr(bipy)_3]^{2+}$ (*cf.* Eq. (13)).

The effect of the oxidant $[Cr(H_2O)_2(bipy)_2]^{3+}$ on the reaction of Eq. (13) will be ruled out if the relation

$$k_6[Cr(H_2O)_2(bipy)_2{}^{3+}] \ll k_1[Co(NH_3)_6{}^{3+}] \qquad (20)$$

holds under the present experimental conditions. The value of k_6 in Eq. (16) is estimated to be *ca.* 10 M^{-1} s^{-1} from the assumed value of k_5 and the values of the reversible half-wave potentials of $[Cr(bipy)_3]^{3+}$ and $[Cr(H_2O)_2(bipy)_2]^{3+}$ obtained polarographically by Baker and Mehta,[9] and the concentration of $[Cr(H_2O)_2(bipy)_2]^{3+}$ is estimated to be *ca.* 10^{-4} M since its formation predominantly takes place *via* the reaction of Eq. (15). Since the concentration of $[Co(NH_3)_6]^{3+}$ is at least *ca.* 10^{-3} M under the large excess of the oxidant and the value of k_1 is assumed to be at least of the order of 10^2 M^{-1} s^{-1},[6] the magnitude of the right-hand side of Eq. (20) amounts to at least *ca.* 100 times that of the left-hand side of the equation. Thus it seems that the backward reaction of Eq. (16) does not affect the reaction of Eq. (13).

The effect of the backward reaction of Eq. (16) (k_6 path) on the dissociation (k_2 path) can also be neglected for the reason that the relation

$$k_6[Cr(H_2O)_2(bipy)_2{}^{3+}] \ll k_2 \qquad (21)$$

holds, because the value of k_2 is estimated to be of the order of 10^{-1} s^{-1}.[7,9] Thus the rate constant k_2 is not affected by the backward reaction of Eq. (16).

Equations (20) and (21) seem to hold similarly in the slight excess of $[Co(NH_3)_6]^{3+}$, since k_1 and k_2 remain constant in a wide concentration range (Table 5). It is concluded that the reaction of $[Cr(bipy)_3]^{2+}$ with $[Co(NH_3)_6]^{3+}$ proceeds *via* the processes of both the direct oxidation of the former with the latter (second-order k_1 path) and the dissociation of the former to $[Cr(H_2O)_2(bipy)_2]^{2+}$ (first-order k_2 path) followed by the rapid oxidation with $[Co(NH_3)_6]^{3+}$; and that Eq. (9) assumed experimentally is adequate for expressing the rate law of the present system. These relationships and the rate law might hold also for the system $[Cr(phen)_3]^{2+}$–$[Co(NH_3)_6]^{3+}$.

A comparison of the rate constants is shown in Table 6. The rate constants for the dissociation of $[Cr(bipy)_3]^{2+}$ have been reported[7,9] (k_2 in Table 6). The values coincide with each other, in spite of the different medium and different ionic strength, and both are greater than ours. Although the value reported by Candlin, Halpern, and Trimm[7] was obtained by a preliminary experiment and thus a detailed discussion is not possible, the greater value in perchlorate medium as compared with that in chloride medium may be interpreted as being due to a salt effect. Both k_{obs}[6] and k_2[7] in the perchlorate medium are about three times those in the chloride medium. These rate constants (k_{obs} and k_2) might be subjected to the salt effect to the same extent. A detailed discussion cannot be presented, since k_{obs} involves k_1. On the other hand, the result for k_2 obtained by Baker and Mehta[9] can be discussed somewhat in detail. They measured the rate of dissociation of $[Cr(bipy)_3]^{2+}$ by following polarographically the decrease in the diffusion current of $[Cr(bipy)_3]^{3+}$ coexisting in solution. They dealt with the reaction on the assumption that the forward re-

TABLE 6. RATE CONSTANTS FOR $[Cr(bipy)_3]^{2+}$ AND $[Cr(phen)_3]^{2+}$ SYSTEMS

μ (medium)	Temp (°C)	k_{obs} (M^{-1} s^{-1})	k_1 (M^{-1} s^{-1})	k_2 (s^{-1})	Ref.
$[Cr(bipy)_3]^{2+}$					
0.11 (NaCl)	25	228	180	0.120	a)
0.10 ($NaClO_4$)	25			0.37[b]	7
0.5 (NaCl)	25			0.38[c]	9
0.096(NaCl)	25	180[d]			6
0.20 (NaCl)	25	250[d]			6
0.10 ($NaClO_4$)	24	690[d]			6
0.20 (NaBr)	23	600[d]			6
$[Cr(phen)_3]^{2+}$					
0.20 (NaCl)	25	373	310	0.630	a)

a) This work. Oxidation with $[Co(NH)_3)_6]^{3+}$. b) Oxidation with $[Co(PO_4)(NH_3)_5]$. c) Reduction of $[Cr(bipy)_3]^{3+}$ with $[Cr(bipy)_3]^{2+}$ followed polarographically. d) Rate data reported are not of the rate constants k_1's but of the apparent rate constants k_{obs}'s defined in the present paper, since the dissociation path in Ref. 6 was not taken into consideration.

action of Eq. (16) proceeds faster than both its backward reaction and the reaction in either direction in Eq. (14), in which the dissociation is the rate-determining step. The assumption should be valid for the reaction in the bulk of the solution. However, the rate constant for the dissociation (k_2) cannot be obtained polarographically unless the rate of diffusion of the depolarizer, $[Cr(bipy)_3]^{3+}$, to the surface of the dropping mercury electrode is greater than that of the reduction of $[Cr(bipy)_3]^{3+}$ with $[Cr(H_2O)_2(bipy)_2]^{2+}$ (Eq. (16)). Otherwise, the consumption of $[Cr(bipy)_3]^{3+}$ during the course of diffusion causes a depression in the concentration of the depolarizer on the electrode surface, leading to the overestimation of the decrease in the bulk concentration. In fact the rate of diffusion does not seem to be so great as that of the reduction of $[Cr(bipy)_3]^{3+}$ with $[Cr(H_2O)_2(bipy)_2]^{2+}$.[16] However, Baker and Mehta ignored the diffusion term leaving the kinetic term, making their treatment inconsistent. Thus, the value 0.38 s^{-1} they obtained must have been overestimated. The greater value, as compared with the present value, cannot be explained either by considering the difference in the ionic strength.

The increasing rates with increase in ionic radii for anions ($Cl^- < Br^- < ClO_4^-$) of the media are considered to be largely due to the salt effect (*cf.* k_{obs} in Table 6). However, the apparent rate constants (k_{obs}) involving the dissociation rate constant k_2 are not necessarily well suited for comparing with each other. A detailed discussion should be based on the rate constant k_1 obtained under various conditions of ionic strengths and media.

The second-order rate constant for $[Cr(phen)_3]^{2+}$ is *ca.* 1.7 times greater than that for $[Cr(bipy)_3]^{2+}$, although there is a difference in ionic strength (*cf.* k_1 in Table 6). The greater rate for $[Cr(phen)_3]^{2+}$ cannot be explained by the tunneling effect as in the case of the reaction of $[Co(NH_3)_6]^{3+}$ or $[Co(en)_3]^{3+}$ (en denotes ethylenediamine) with $[Cr(bipy)_3]^{2+}$,[6] because of the greater size of the phenanthroline complex as compared with the bipyridine complex. The greater reactivity is in accord with the results obtained by Ford-Smith and Sutin[17] and Sutin and Gordon,[18] who reported the rate constants for the systems Fe^{2+}–$[Fe(bipy)_3]^{3+}$ and Fe^{2+}–$[Fe(phen)_3]^{3+}$ in 0.5 M $HClO_4$ at 25.0 °C to be 2.7×10^4 M^{-1} s^{-1} [17,18] and 3.7×10^4 M^{-1} s^{-1},[17] respectively. The ratio of the rate constant reported for the phenanthroline complex to that for the bipyridine complex is *ca.* 1.4, which agrees with ours, if the difference in ionic strength for Cr(II) complexes is taken into consideration. The greater reactivity for $[Cr(phen)_3]^{2+}$ is ascribed to the effect of an electron on the metal t_{2g} orbital spreading itself around on the ligand π orbital through the π interaction. The reaction is facilitated in spite of the larger size of the complex. The reactivity for these systems is caused by the electron conductivity of the ligand in the π-conjugate complex. For a complex without π-conjugation, such as Cr^{2+}, the slow rate for the oxidation with $[Co(NH_3)_6]^{3+}$ *via* the outer-sphere mechanism (8.8×10^{-4} M^{-1} s^{-1}, $\mu=0.40$, at 25.0 °C)[2] can be explained by the poor electron conductivity of the water molecule attached.

From the temperature dependence of the rate constants k_1 and k_2 and of the apparent rate constant k_{obs}, the activation parameters for $[Cr(bipy)_3]^{2+}$ and $[Cr(phen)_3]^{2+}$ systems were evaluated by transition-state theory according to:

$$k = \frac{\boldsymbol{k}T}{h}\, e^{-\Delta H^{\ddagger}/RT} e^{\Delta S^{\ddagger}/R}$$

The results are shown in Table 7, together with those of other investigators. The activation parameters for k_{obs} are in excellent agreement with those obtained by Zwickel and Taube,[6] considering the difference in ionic strengths. It is concluded that the rate constants they obtanied correspond to the apparent rate constant (k_{obs}) defined in the present paper. Since the reaction proceeds in two paths as expressed by Eq. (9), the parameters for both paths should be obtained (Table 7).

TABLE 7. KINETIC AND ACTIVATION PARAMETERS FOR THE REACTIONS OF $[Cr(bipy)_3]^{2+}$ AND $[Cr(phen)_3]^{2+}$ WITH $[Co(NH_3)_6]^{3+}$ AT 25 °C

μ (medium)	Reaction path	Rate constant (M^{-1} s^{-1})	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (e.u.)	$\Delta G^{\ddagger}$ (kcal/mol)	Ref.
$[Cr(bipy)_3]^{2+}$						
0.11(NaCl)	k_{obs}	228	10.3	−13	14.2	a)
0.20(NaCl)	k_{obs}	250	9.9	−14	14.1	6
0.05(NaCl)	k_{obs}	113	11.3	−10	14.3	6
0.01(NaCl)	k_{obs}	40	13.0	− 9	15.7	6
0.11(NaCl)	k_1	180	7.5	−23	14.4	a)
0.11(NaCl)	k_2	0.120[b]	17.2	− 5	18.6	a)
0.5 (NaCl)	k_2	0.38[b]	22.6[c]	+13[d]	18.1	9[e]
$[Cr(phen)_3]^{2+}$						
0.20(NaCl)	k_{obs}	373	11.5	− 8	13.9	a)
0.20(NaCl)	k_1	310	8.2	−20	14.2	a)
0.20(NaCl)	k_2	0.630[b]	21.2	+12	17.6	a)

a) This work. b) For k_2 paths, the rate constant is in s^{-1}. c) Value for the activation energy, E_a. d) The value was not reported by Baker and Mehta,[9] so it is cited from Ref. 14a. e) *Cf.* footnote c), Table 6.

It is reasonable to consider that a similar mechanism is operative for the oxidation of $[Cr(bipy)_3]^{2+}$ and of $[Cr(phen)_3]^{2+}$ (k_1 in Table 7), because activation enthalpies (7.5 kcal/mol and 8.2 kcal/mol) and activation entropies (−23 e.u. and −20 e.u.) obtained for respective complexes are of similar magnitude. However, as the activation entropies, $\Delta S^{\ddagger}$'s, for outer-sphere reactions are sensitive to the medium, the values obtained at different ionic strengths cannot be compared directly with each other. Nevertheless, the values of the activation entropies obtained for $[Cr(bipy)_3]^{2+}$ and $[Cr(phen)_3]^{2+}$ indicate that the total charges on the transition complexes are between +4 and +5.[19] Discussions should be carried out with the use of the thermodynamic activation parameters.

The greater activation enthalpy for the k_1 path of $[Cr(phen)_3]^{2+}$ as compared with that of $[Cr(bipy)_3]^{2+}$ (Table 7) is interpreted as being due to the greater stability in the ground state of the former.

It should be noted that the coincidence of the $\Delta G^{\ddagger}$ value calculated from the results by Baker and Mehta[9] with ours for the k_2 path occurs as a result of the cancellation of the overestimated $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values. Although the overestimation of the activation parameters cannot be easily interpreted, it might be caused by a greater overestimation of the rate constant for the dissociation at a higher temperature, since the temperature dependence of the diffusion rate is not as significant as that of the reduction rate of $[Cr(bipy)_3]^{3+}$.

Conclusion

The oxidation reaction of $[Cr(bipy)_3]^{2+}$ and of $[Cr(phen)_3]^{2+}$ complexes with $[Co(NH_3)_6]^{3+}$ ion proceeds in two paths through the outer-sphere mechanism: direct oxidation of $[Cr(bipy)_3]^{2+}$ or $[Cr(phen)_3]^{2+}$ (second-order reaction); oxidation of $[Cr(H_2O)_2(bipy)_2]^{2+}$ or $[Cr(H_2O)_2(phen)_2]^{2+}$ formed by the dissociation of $[Cr(bipy)_3]^{2+}$ or $[Cr(phen)_3]^{2+}$, the dissociation (first-order reaction) being rate-determining for the oxidation of the dissociated complex. The rate constants of the paths for these complexes were obtained by means of analogue computer simulation procedures. The activation parameters for the direct oxidation and dissociation processes of each of these complexes were also obtained.

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