October, 1976] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49 (10), 2743—2747 (1976) 2743

A Kinetic Study of the Chromium(II) Reduction of Several (Amino acid)pentaamminecobalt(III) Complexes

Hiroshi Ogino, Keiichi Tsukahara, and Nobuyuki Tanaka

Department of Chemistry, Faculty of Science, Tohoku University, Aoba, Aramaki, Sendai 980

(Received April 30, 1976)

A kinetic study of the chromium(II) reduction of (O-bonded amino acid)pentaamminecobalt(III) complexes has been carried out in acid solutions. The second-order rate constants in $M^{-1}\,s^{-1}$ (1 M=1 mol dm^{-3}) at 25 °C and I=1.0 M ($NaClO_4$) for α-alanine, phenylalanine, α-aminoisobutyric acid, β-alanine, β-aminobutyric acid, γ-aminobutyric acid, and ε-aminohexanoic acid complexes are 1.8×10^{-2}, 1.5×10^{-2}, 2.4×10^{-3}, 7.5×10^{-2}, 5.0×10^{-2}, 1.22×10^{-1}, and 1.49×10^{-1} respectively. The values of ΔH^* lie in the range of 6.4—7.7 kcal mol^{-1} (1 cal=4.184 J), and those of ΔS^*, in the range of −42—−37 cal $K^{-1}\,mol^{-1}$, except for the α-aminoisobutyric acid complex, the ΔH^* and ΔS^* values of which are 11.4 kcal mol^{-1} and −32 cal $K^{-1}\,mol^{-1}$ respectively. The role of the amino acid ligands in the inner-sphere electron-transfer reactions is discussed.

The chromium(II) reduction of a number of carboxylatopentaamminecobalt(III) complexes has been known to proceed predominantly through an inner-sphere mechanism.[1,2] In these reactions, the steric crowding of the alkyl groups influences the electron-transfer rate significantly. The chromium(II) reduction of the pentaammineglycinecobalt(III) complex has also been investigated by several researchers[3–5] and found to proceed predominantly through an inner-sphere mechanism. The reduction rate of this complex was found to be smaller than that of the acetatopentaamminecobalt(III) complex. This fact was interpreted in terms of the difference in the positive charge on the complexes.

In this work, the rate of the chromium(II) redution of a number of (O-bonded amino acid)pentaamminecobalt(III) complexes was measured in acid solutions in order to reveal the factors which control the electron-transfer reaction rate. The abbreviations used in this work are as follows: amino acid=amH, $^-O_2CCH_2NH_3^+$ (glycine)=glyH, $^-O_2CCH(CH_3)NH_3^+$ (α-alanine)=alaH, $^-O_2C(CH_2)_2NH_3^+$ (β-alanine)=balaH, $^-O_2CCH(CH_2C_6H_5)NH_3^+$ (phenylalanine)=pheH, $^-O_2CCH_2CH(CH_3)NH_3^+$ (β-aminobutyric acid)=babH, $^-O_2CC(CH_3)_2NH_3^+$ (α-aminoisobutyric acid)=aibH, $^-O_2C(CH_2)_3NH_3^+$ (γ-aminobutyric acid)=gabH, and $^-O_2C(CH_2)_5NH_3^+$ (ε-aminohexanoic acid)=ahH.

Experimental

Reagents. (O-bonded amino acid)pentaamminecobalt(III) complexes were prepared as perchlorates by the method reported previously.[6,7] The $[Co(babH)(NH_3)_5](ClO_4)_3$ and $[Co(ahH)(NH_3)_5](ClO_4)_3$ complexes were purified by the use of an SP-Sephadex C-25 column. Each amino acid complex adsorbed on the column moved faster than aquapentaamminecobalt(III) ions with an 0.3 M $NaClO_4$ solution at pH 3 (1 M=1 mol dm^{-3}). Table 1 gives the analytical data of the complexes used in this work.

All the solutions used for the measurements were prepared from redistilled water. A solution of hexaaquachromium(III) perchlorate was prepared from sodium dichromate as has been reported previously.[8] A chromium(II) perchlorate solution was prepared by the reduction of the hexaaquachromium(III) perchlorate with a zinc amalgam in a nitrogen atmosphere. The hydrogen-ion concentration of the chromium(II) solution was determined by a method reported previously.[9,10] A sodium perchlorate solution was prepared by neutralizing a primary standard sodium carbonate solution with perchloric acid.

Product Analyses. The products of the reactions of Cr^{2+} ions with $Co(alaH)(NH_3)_5{}^{3+}$ and $Co(aibH)(NH_3)_5{}^{3+}$ ions were examined. After the reaction had been quenched by the introduction of air into the system, the solution was cooled and passed through an SP-Sephadex C-25 column chilled below 5 °C with a water-jacket. The colored species were adsorbed on the column in four bands: pink, bluish violet, red, and green from the bottom to the top of the column. The pink species was eluted with an 0.1 M $HClO_4$–0.1 M $NaClO_4$ solution and was identified as Co^{2+} ions. The bluish violet species was eluted with an 0.1 M $HClO_4$–0.3 M $NaClO_4$ solution and was found to be chromium(III) species. The visible spectrum of the species was similar to $Cr(H_2O)_6{}^{3+}$, but not identical. Therefore, the species was considered to be $Cr(amH)(H_2O)_5{}^{3+}$ or a mixture of $Cr(amH)(H_2O)_5{}^{3+}$ and $Cr(H_2O)_6{}^{3+}$. The red species was eluted with an 0.1 M $HClO_4$–0.3 M $NaClO_4$ solution and identified as

Table 1. Analytical data of the cobalt(III) complexes used in this work

Compound	Calcd (%)			Found (%)		
	C	H	N	C	H	N
$[Co(O_2CCH_2NH_3)(NH_3)_5](ClO_4)_3$	4.49	4.14	15.69	4.37	4.36	15.75
$[Co(O_2CCH(CH_3)NH_3)(NH_3)_5](ClO_4)_3$	6.78	4.18	15.81	6.77	4.39	15.93
$[Co(O_2CC(CH_3)_2NH_3)(NH_3)_5](ClO_4)_3$	8.80	4.44	15.41	8.60	4.59	15.14
$[Co(O_2C(CH_2)_2NH_3)(NH_3)_5](ClO_4)_3$	6.78	4.18	15.81	6.46	4.31	15.80
$[Co(O_2C(CH_2)_3NH_3)(NH_3)_5](ClO_4)_3$	8.80	4.44	15.41	9.08	4.62	15.23
$[Co(O_2C(CH_2)_5NH_3)(NH_3)_5](ClO_4)_3\cdot2H_2O$	11.82	5.30	13.79	12.36	5.03	13.32
$[Co(O_2CCH(CH_2C_6H_5)NH_3)(NH_3)_5](ClO_4)_3\cdot H_2O$	17.27	4.52	13.43	17.63	4.61	13.37
$[Co(O_2CCH_2CH(CH_3)NH_3)(NH_3)_5](ClO_4)_3$	8.80	4.44	15.41	8.82	4.62	15.20

$Co(amH)(NH_3)_5^{3+}$. The green species was eluted with an 0.1 M $HClO_4$–0.9 M $NaClO_4$ solution and identified as $(H_2O)_4Cr(OH)_2Cr(H_2O)_4^{4+}$, which was considered to have been derived by the air oxidation of Cr^{2+} ions.[11,12]

The chromium content was determined spectrophotometrically in the form of CrO_4^{2-} after oxidation with an alkaline hydrogen peroxide solution. The cobalt(II) content was determined spectrophotometrically as $Co(NCS)_4^{2-}$ in 50% acetone. The cobalt(III) complexes were reduced to cobalt(II) with a zinc amalgam and then subjected to the determination of the cobalt(II) as $Co(NCS)_4^{2-}$. From the results of the product analyses, it was confirmed that 1 mol of Cr^{2+} is consumed per mole of the $Co(alaH)(NH_3)_5^{3+}$ or $Co(balaH)(NH_3)_5^{3+}$ complex.

The amounts of amH and Co^{2+} released by the Cr^{2+} reduction were determined for the reactions of $Co(alaH)(NH_3)_5^{3+}$ and $Co(aibH)(NH_3)_5^{3+}$. The following procedures were employed: the reaction mixture was poured into an SP-Sephadex column. The solution which was passed through the column was reserved. The effluent was collected until the Co^{2+} band almost reached the bottom of the column by eluting with a cold 0.1 M $HClO_4$–0.1 M $NaClO_4$ solution. The solution reserved and the effluent were then combined and alkalified with NaOH. The solution was heated on a boiling-water bath for half an hour to expel the ammonia and then acidified with $HClO_4$. The alaH content of the solution was determined spectrophotometrically with ninhydrin, as has been reported by Yemm and Cocking.[13] The aibH content was determined by pH titration under nitrogen with a standard NaOH solution. The pH values were measured with a Hitachi-Horiba F-5 pH meter.

Kinetic Measurments. Solutions containing a cobalt(III) complex, $NaClO_4$ and $HClO_4$ were added to an optical cell, which was then sealed with a serum cap. After the solution has been purged with nitrogen gas for 15 min, the reaction was initiated by the addition of a Cr^{2+} solution with a syringe. The change in the absorbance with the time was followed at 500 nm with a Hitachi EPS-3 spectrophotometer. The ionic strength of the solution was adjusted to 1.0 M throughout the work, unless otherwise stated. The temperature was controlled by circulating water through the cell holder. The temperature was kept constant within 0.1 °C at each desired temperature.

Results

Determination of the Rate Constants of the Electron-transfer Reactions. The spectral changes observed during the reaction of Cr^{2+} with the pentaamminecobalt(III) complex of balaH, gabH, ahH, or babH gave three isosbestic points within the range of 340—600 nm. The electron-transfer reactions of Cr^{2+} with the $Co(amH)(NH_3)_5^{3+}$ complexes are considered to proceed predominantly through an inner-sphere mechanism; this is on the basis of the earlier observation of the reaction of $Co(glyH)(NH_3)_5^{3+}$:[5)]

$$Cr^{2+} + Co(amH)(NH_3)_5^{3+} + 5H^+ \rightarrow Cr(amH)(H_2O)_5^{3+} + Co^{2+} + 5NH_4^+ \qquad (1)$$

The rate of the reaction of Cr^{2+} with the pentaamminecobalt(III) complex ligating alaH, pheH, or aibH was smaller than that of the complex ligating balaH, gabH, ahH, or babH, and in the cases of the former complexes the isosbestic points collapsed with the time, as is shown in Fig. 1. This may be attributed to the occurrence of the Cr^{2+}-catalyzed aquation of $Cr(amH)(H_2O)_5^{3+}$:

$$Cr(amH)(H_2O)_5^{3+} + Cr^{2+} \rightarrow Cr^{2+} + amH + Cr(H_2O)_6^{3+} \qquad (2)$$

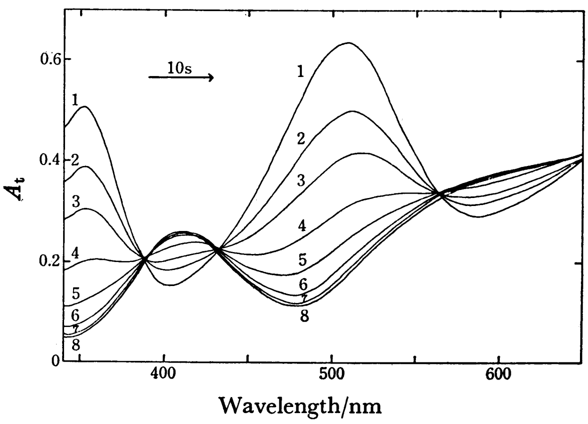


Fig. 1. The spectral changes during the reaction of Cr^{2+} with $Co(alaH)(NH_3)_5^{3+}$ at $[Cr^{2+}]_0=0.100$ M, $[Co(III)]_0=9.59\times10^{-3}$ M, $[H^+]=0.100$ M, 35 °C, and $I=1.0$ M ($NaClO_4$): 1, 20 s; 2, 2 min 20 s; 3, 4 min 20 s; 4, 8 min 20 s; 5, 13 min 20 s; 6, 20 min 20 s; 7, 29 min 20 s; 8, 39 min 20 s after the reaction. Times given are for start of scan at 340 nm.

If Reaction 1 obeys this rate equation:

$$-\frac{d[Co(III)]}{dt} = k[Co(III)][Cr^{2+}] \qquad (3)$$

Equation 4 can be derived thus:

$$\log\frac{\varepsilon_{Co(III)}l([Cr^{2+}]_0-[Co(III)]_0)-\varepsilon_{Cr(III)}l[Cr^{2+}]_0+A_t}{A_t-A_\infty} = \frac{[Cr^{2+}]_0-[Co(III)]_0}{2.303}kt + \log\frac{[Cr^{2+}]_0}{[Co(III)]_0} \qquad (4)$$

where $[Cr^{2+}]_0$ and $[Co(III)]_0$ indicate the initial concentrations of Cr^{2+} and $Co(amH)(NH_3)_5^{3+}$ respectively. A_t and A_∞ denote the absorbances at time t and infinity respectively. The symbols, $\varepsilon_{Co(III)}$ and $\varepsilon_{Cr(III)}$, are the molar absorption coefficients of $Co(amH)(NH_3)_5^{3+}$ and $Cr(amH)(H_2O)_5^{3+}$ at 500 nm respectively, and l denotes the optical path length. The plots of the left-hand side of Eq. 4 *vs.* t for each system expect that of the aibH complex gave a linear relation for at least three half-lives. The second-order rate constant, k, was determined from the slope of this straight line. In these calculations, the values of $\varepsilon_{Cr(III)}$ were estimated from the values of A_∞. Equation 4 held even in the reactions for the alaH and pheH complexes. This may be because of the following reasons: (a) Reaction 2 is much slower than 1. (b) The ε value of $Cr(amH)(H_2O)_5^{3+}$ is quite similar to that of $Cr(H_2O)_6^{3+}$ at the wavelegth used for the measurements (500 nm). (c) The $\varepsilon_{Cr(III)}$ value is much smaller than the $\varepsilon_{Co(III)}$ value at 500 nm. In the reaction of Cr^{2+} with $Co(aibH)(NH_3)_5^{3+}$, however, the accurate determination of the values of A_∞ was difficult due to the considerable contribution of Reaction 2 to Reaction 1. Therefore, the method of Guggenheim[14] was employed.

Kinetic measurements were carried out under various concentrations of Cr^{2+} (0.05—0.1 M), Co(amH)-

Table 2. Rate constants of the reaction of Cr^{2+} with $Co(amH)(NH_3)_5^{3+}$

amH	Temp/°C	10^2 $k^{a)}$/M^{-1} s^{-1}
alaH	25.0	1.8±0.1
	34.5	2.6±0.1
	40.5	3.4±0.1
	45.0	4.0±0.1
aibH	25.0	0.24±0.01
	34.5	0.43±0.02
	40.0	0.63±0.01
	44.8	0.82±0.01
balaH	24.8	7.5±0.3
	30.0	9.5±0.1
	35.0	11.7±0.1
	39.8	14.0±0.1
gabH	25.3	12.2±0.2
	34.7	18.5±0.7
	43.8	24.3±0.1
ahH	25.3	14.9±0.2
	35.5	23.5±0.3
	44.7	34.7±0.3
babH	25.0	5.0±0.1
	35.5	7.7±0.2
	44.7	11.8±0.3
pheH	25.0	1.5±0.1
	35.0	2.2±0.1
	44.0	3.5±0.1

a) Each value is the average of two to eleven determinations. The uncertainty is the average deviation.

$(NH_3)_5^{3+}$ (5×10^{-3}—1×10^{-2} M), and hydrogen ions (0.1—0.5 M). The second-order rate constants (k) were found to be independent of the concentration of the hydrogen ions. The rate constants at various temperatures are given in Table 2, and the kinetic parameters, in Table 3, along with the data obtained by other researchers.

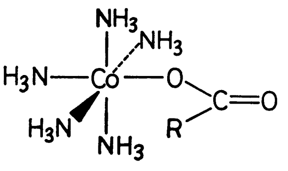
Cr^{2+}-catalyzed Aquation of $Cr(amH)(H_2O)_5^{3+}$. The analytical results for Co^{2+} and amH released by the Cr^{2+} reduction are summarized in Table 4, which shows that the amount of amH is always smaller than that of Co^{2+} and that it increases with the reaction time. These findings support the consideration that the mechanism of the electron-transfer reactions is predominantly of the inner-sphere type[16] and indicate that the prolonged contact of $Cr(amH)(H_2O)_5^{3+}$ with Cr^{2+} causes Reaction 2 to a considerable extent. If the reaction between Cr^{2+} and $Co(aibH)(NH_3)_5^{3+}$ proceeds exclusively through an inner-sphere mechanism, the rate constant of the Cr^{2+}-catalyzed aquation of $Cr(aibH)(H_2O)_5^{3+}$ is estimated from the data given in Table 4 to be approximately 7×10^{-5} M^{-1} s^{-1}.

Discussion

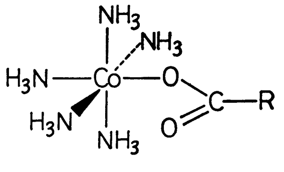
The data given in Table 3 show the following facts: (a) The substitution of methyl groups or a benzyl group for α hydrogens of glyH causes a decrease in the rate of the electron-transfer reaction (compare the k values of glyH, alaH, aibH, and pheH complexes). (b) The rate of the electron-transfer reaction increases with the increase in the number of methylene groups between carboxylate and ammonium groups in amH (compare the k values of glyH, balaH, gabH, and ahH complexes). (c) The ΔH^* values as well as the ΔS^* values of all the complexes except the aibH complex are quite similar to each other.

It has been shown that cobalt(III) ammine complexes ligating alkyl carboxylate ligands were reduced by Cr^{2+} at carbonyl oxygen atoms.[17—19] Fact (a) indicates that the substitution of bulky groups for α hydrogens of glyH hinders the C=O attacking by Cr^{2+}. It is known that the rates of the reduction of N-methyl-substituted glycinepentaamminecobalt(III) ions by Cr^{2+} decrease with the increase in the number of the N-methyl groups.[5] The data given in Table 3 indicate that the alkyl substitution on the methylene group in glyH hinders the C=O attack more seriously than that on the ammonium nitrogen does. This result can be understood when the steric crowding around the C=O group is considered.

The steric crowding around the C=O group in $Co(O_2C(CH_2)_nNH_3)(NH_3)_5^{3+}$ may increase as the number of methylene groups between carboxyl and ammonium groups increases; hence, the rate of the electron-transfer reactions would decrease with the increase in the number of methylene groups. However, Fact (b) is opposed to this expectation. The discrepancy may be understood by considering electrostatic repulsions between the ammonium group, the cobalt(III) center, and the attacking Cr^{2+} ion. The positively charged ammonium group will tend to be separated from the positively charged cobalt(III) center due to the electrostatic repulsion. Therfore, the charge separation between the ammonium group and the cobalt(III) center becomes larger as the methylenic chain of the amH becomes longer. The approach of the positively charged Cr^{2+} ion to the C=O moiety becomes easier as the number of methylene groups of the amH increases. Balahura and Jordan made it clear that the conformation of the coordinated formate ion in $Co(O_2CH)(NH_3)_5^{2+}$ is of Form I (R=H).[19]



I



II

For other cases such as with the acetato complex, they claimed that Form II would be greatly favored by steric consideration. For the conformation of the amH in $Co(amH)(NH_3)_5^{3+}$, Form II would be favored over Form I. When this conformational situation and the electrostatic repulsion between the ammonium group and the cobalt(III) center are considered, molecular models indicate that the $-(CH_2)_nNH_3^+$ group takes a severely restricted orientation and that the steric crowding around the C=O group is slightly altered

TABLE 3. KINETIC DATA FOR THE REACTION OF Cr^{2+} WITH $Co(amH)(NH_3)_5^{3+}$

amH $(pK_a)^{a)}$	$\frac{k}{M^{-1}\,s^{-1}}$	$\frac{\Delta H^{*\,d)}}{kcal\,mol^{-1}}$	$\frac{\Delta S^{*\,d)}}{cal\,K^{-1}\,mol^{-1}}$	Ref.
$\overset{-}{O}OCCH_2\overset{+}{N}H_3$	$0.064^{b)}$	7.7 ± 0.2	-38 ± 1	5
(2.35)	$0.064^{c)}$			This work
$\overset{-}{O}OC(CH_2)_2\overset{+}{N}H_3$ (3.55)	$0.075^{c)}$	7.4 ± 0.6	-39 ± 2	This work
$\overset{-}{O}OC(CH_2)_3\overset{+}{N}H_3$	$0.122^{c)}$	9.9	−30	4
(4.03)	$0.122^{c)}$	6.4 ± 0.3	-41 ± 1	This work
$\overset{-}{O}OC(CH_2)_5\overset{+}{N}H_3$ (4.43)	$0.15^{c)}$	7.7 ± 0.1	-37 ± 1	This work
$\overset{-}{O}OCCH_2\overset{+}{N}H_2(CH_3)$ (2.35)	$0.044^{b)}$	8.0 ± 0.2	-38 ± 1	5
$\overset{-}{O}OCCH_2\overset{+}{N}H(CH_3)_2$ (2.15)	$0.038^{b)}$	7.5 ± 0.2	-40 ± 1	5
$\overset{-}{O}OCCH_2\overset{+}{N}(CH_3)_3$ (1.84)	$0.016^{b)}$	7.7 ± 0.2	-41 ± 1	5
$\overset{-}{O}OCCH_2CH(CH_3)\overset{+}{N}H_3$ (3.55)	$0.050^{c)}$	7.3 ± 0.1	-40 ± 1	This work
$\overset{-}{O}OCCH(CH_3)\overset{+}{N}H_3$	$0.049^{c)}$	8.0 ± 0.3	-37 ± 1	15
(2.34)	$0.018^{c)}$	7.4 ± 0.1	-42 ± 1	This work
$\overset{-}{O}OCCH(CH_2C_6H_5)\overset{+}{N}H_3$ (2.20)	$0.015^{c)}$	7.5 ± 0.2	-42 ± 1	This work
$\overset{-}{O}OCC(CH_3)_2\overset{+}{N}H_3$ (2.36)	$0.0024^{c)}$	11.4 ± 0.2	-32 ± 1	This work

a) 25 °C and $I=0$ M. The K_a value is defined for this equilibrium: $amH_2^+ \rightleftharpoons amH + H^+$. The data for pK_a are taken from A. E. Martell and L. G. Sillén, "Stability Constants, Supplement No. 1," The Chemical Society, London (1971). b) 25 °C and $I=1.0$ M ($LiClO_4$). c) 25 °C and $I=1.0$ M ($NaClO_4$). d) The uncertainty is the standard deviation from the least-squares fit for the activation parameters. The computations were carried out on a NEAC-2200 Model 700 at the Computer Center at Tohoku University. 1 cal = 4.184 J.

TABLE 4. THE ANALYTICAL RESULTS FOR Co^{2+} AND amH RELEASED BY THE REACTION OF Cr^{2+} WITH $Co(amH)(NH_3)_5^{3+}$

Complex	The initial concentrations of the reactants		Reaction time/min	The concentrations of the products		Product ratio
	$[Cr^{2+}]_0\times10^3$/M	$[Co(III)]_0\times10^3$/M		$[Co^{2+}]\times10^3$/M	$[amH]\times10^3$/M	$\frac{[amH]}{[Co^{2+}]}$
$Co(aibH)(NH_3)_5^{3+\ a)}$	103	21.3	90	11.9 ± 0.6	3.0 ± 0.2	0.25 ± 0.03
	103	30.0	90	18.6 ± 0.9	3.5 ± 0.3	0.19 ± 0.03
	103	29.6	180	20.3 ± 1.0	8.6 ± 0.4	0.42 ± 0.04
$Co(alaH)(NH_3)_5^{3+\ b)}$	100	9.87	5	6.19 ± 0.31	<0.25	<0.04
	100	9.59	50	10.0 ± 0.5	2.5 ± 0.2	0.25 ± 0.03

a) At 25 °C, $I=0.7$ M ($NaClO_4$), and $[H^+]=0.090$ M. b) At 35 °C, $I=1.0$ M ($NaClO_4$), and $[H^+]=0.10$ M.

by the increase in the methylenic chain length. It should also be noted that the variation in the pK_a values of amH may influence the rate constants. The pK_a values of the amH are given in Table 3. The rate constants of the pentaamminecobalt(III) complexes ligating sarcosine, balaH, gabH, and ahH increase with the increase in the pK_a values. Molecular models indicate that the steric crowding around the C=O groups of these complexes is comparable with respect to the attack on the C=O groups by Cr^{2+}. The increase in pK_a values may cause the increase in the electron density of the carboxylate group, which, in turn, may make the attack of the carboxylate position by Cr^{2+} easier.

The similarity in the activation parameters among all the complexes studied except the aibH complex indicates that the reactions take place by the same mechanism. Although the ΔH^* and ΔS^* values of the aibH complex are larger than those of the other complexes by 4—5 kcal mol^{-1} and 5—10 cal K^{-1} mol^{-1} respectively, the product analyses indicated that the mechanism for the aibH complex was predominantly

$(NH_3)_5CoOOCCH_3^{2+}$
0.35[a)]

$(NH_3)_5CoOOCCH_2CH_3^{2+}$
0.14[b)]

$(NH_3)_5CoOOC(CH_2)_2CH_3^{2+}$
0.08[c)]

$(NH_3)_5CoOOCCH_2NH_3^{3+}$
0.064[d)]

$(NH_3)_5CoOOC(CH_2)_2NH_3^{3+}$
0.075[e)]

$(NH_3)_5CoOOC(CH_2)_3NH_3^{3+}$
0.122[e)]

$(NH_3)_5CoOOC(CH_2)_5NH_3^{3+}$
0.15[e)]

Scheme 1. Comparison of the second-order rate constants (in $M^{-1} s^{-1}$) of the reactions of Cr^{2+} with $Co(O_2C(CH_2)_nCH_3)(NH_3)_5^{2+}$ and $Co(O_2C(CH_2)_nNH_3)(NH_3)_5^{3+}$ at 25 °C and $I = 1$ M, unless otherwise indicated.

a) Ref. 2 and M. B. Barrett, J. H. Swinehart, and H. Taube, *Inorg. Chem.*, **10**, 1983 (1971). b) E. S. Gould, *J. Am. Chem. Soc.*, **88**, 2983 (1966); at 25 °C and $I = 1.5$ M. c) H. Taube, *J. Am. Chem. Soc.*, **77**, 4481 (1955). d) Ref. 5. e) This work.

of an inner-sphere type.

The second-order rate constant of the reactions of Cr^{2+} with some pentaamminecobalt(III) complexes ligating $^{-}O_2C(CH_2)_nCH_3$ and $^{-}O_2C(CH_2)_nNH_3^+$ ligands are compared in Scheme 1. The rate of the carboxylato complexes decreases with the increase in the methylenic chain length. This trend is in contrast with that observed for the amH complexes. Although the positive charge of the butyrato complex is less than those of the amH complexes, the rate of the former complex is smaller than those of $Co(gabH)(NH_3)_5^{3+}$ and $Co(ahH)(NH_3)_5^{3+}$. As has been mentioned above, the $-(CH_2)_nNH_3^+$ group takes a severely restricted orientation and the ammonium group is located apart from the C=O moiety. On the other hand, the alkyl group, which is electrically neutral, is able to wander about in the vicinity of the C=O moiety in the same complex ion. Therefore, the alkyl group may hinder increasingly the attack on the C=O group by Cr^{2+} with the increase in the methylenic chain length.

References

1) H. Taube, "Mechanisms of Inorganic Reactions," Adv. Chem. Ser., Am. Chem. Soc. publ. No. 49 (1965), p. 107.

2) H. Taube and E. S. Gould, *Acc. Chem. Res.*, **2**, 321 (1969).

3) K. D. Kopple and G. F. Svatos, *J. Am. Chem. Soc.*, **82**, 3227 (1960).

4) R. T. M. Fraser, *Inorg. Chem.*, **3**, 1561 (1964).

5) H. Holwerda, E. Deutsch, and H. Taube, *Inorg. Chem.*, **11**, 1965 (1972).

6) J. Fujita, T. Yasui, and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **38**, 654 (1965).

7) Some of the complexes were kindly provided by Professor Kazuko Ogino, College of Medical Sciences, Tohoku University.

8) H. Ogino and N. Tanaka, *Bull. Chem. Soc. Jpn.*, **41**, 1622 (1968).

9) E. L. King and J. A. Neptune, *J. Am. Chem. Soc.*, **77**, 3186 (1955).

10) K. D. Kopple and R. R. Miller, *Inorg. Chem.*, **2**, 1204 (1963).

11) M. Ardon and R. A. Plane, *J. Am. Chem. Soc.*, **81**, 3197 (1959).

12) R. W. Kolaczkowski and R. A. Plane, *Inorg. Chem.*, **3**, 322 (1964).

13) E. W. Yemm and E. C. Cocking, *Analyst*, **80**, 209 (1955).

14) E. A. Guggenheim, *Phil. Mag.*, [7] **2**, 538 (1926).

15) R. Bembi and W. U. Malik, *J. Inorg. Nucl. Chem.*, **37**, 570 (1975).

16) The data given in Table 4 reveal that at least 80% of the electron-transfer reaction between Cr^{2+} and $Co(aibH)(NH_3)_5^{3+}$ proceeds through an inner-sphere path.

17) K. L. Scott and A. G. Sykes, *J. Chem. Soc., Dalton*, **1972**, 1832.

18) S. A. Stritar and H. Taube, *Inorg. Chem.*, **8**, 2281 (1969).

19) R. J. Balahura and R. B. Jordan, *Inorg. Chem.*, **12**, 1438 (1973).