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Syntheses, Characterizations, and Interconversion Reactions of *cis*- and *trans*-Bis(2,4-pentanedionato)diaquachromium(III) Complexes. Application to the Cleavage Reactions of the Chromium–Carbon Bonds in *trans*-(Dichloromethyl and chloromethyl)bis(2,4-pentanedionato)aquachromium(III) Complexes in Aqueous Solutions

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The geometric isomer pair of bis(2,4-pentanedionato)diaquachromium(III) complexes, $[Cr(acac)_2(H_2O)_2]X$ ($X = ClO_4^-, Cl^-$), were prepared and characterized by elemental analysis, electronic spectroscopy, pH titration, and optical resolution. Each isomer in an aqueous solution isomerizes to give an equilibrium mixture of *cis*- and *trans*-$[Cr(acac)_2(H_2O)_2]^+$. The equilibrium constants of the cis–trans isomerization at $I = 0$ M, K = [cis isomer]/[trans isomer], were determined to be 7.7 ± 0.5 at 35 °C, 7.1 ± 0.4 at 45 °C, and 6.7 ± 0.4 at 53 °C. Kinetic measurements were made for the cis–trans isomerization reaction. The reaction followed the first-order rate law. The rate constants of the trans to cis and cis to trans isomerizations at $I = 0$ M were $(1.8 \pm 0.1) \times 10^{-5}$ and $(2.4 \pm 0.3) \times 10^{-6}\ s^{-1}$ at 35 °C and $(2.3 \pm 0.1) \times 10^{-4}$ and $(3.4 \pm 0.4) \times 10^{-5}\ s^{-1}$ at 53 °C, respectively. On the basis of these results, the cleavage reactions of the chromium–carbon bonds in *trans*-$[CrR(acac)_2(H_2O)]$ complexes were investigated in aqueous solutions, where R denotes dichloromethyl and chloromethyl groups. *trans*-$[CrR(acac)_2(H_2O)]$ complexes give *trans*-$[Cr(acac)_2(H_2O)_2]^+$ ions, which isomerize to give an equilibrium mixture of *cis*- and *trans*-$[Cr(acac)_2(H_2O)_2]^+$ ions. In addition to these reactions, formation of $[Cr(acac)(H_2O)_4]^{2+}$ appears to contribute to the net reaction.

Introduction

Balahura and Lewis obtained bis(2,4-pentanedionato)diaquachromium(III) ions, $[Cr(acac)_2(H_2O)_2]^+$, as the product of the electron-transfer reaction of $[Co(acac)_2(en)]^+$ with Cr^{2+} and reported its electronic absorption spectrum.[1-3] Banerjea et al. isolated $[Cr(acac)_2(H_2O)_2]NO_3{\cdot}H_2O$.[4,5] In these papers, however, there is no description on the geometric configuration of $[Cr(acac)_2(H_2O)_2]^+$.

We report here the syntheses and characterizations of *cis*-$[Cr(acac)_2(H_2O)_2]ClO_4$ and *trans*-$[Cr(acac)_2(H_2O)_2]X$ ($X = ClO_4^-, Cl^-$) and the equilibrium and kinetic studies of their isomerization reactions in aqueous solutions. These results are applied to the analysis of the chromium–carbon bond-cleavage reactions of *trans*-$[CrR(acac)_2(H_2O)]$ ($R = CHCl_2, CH_2Cl$), which we have isolated recently by replacing four coordinated water molecules of $[CrR(H_2O)_5]^{2+}$ with two $acac^-$ ions.[6,7] If the chromium–carbon bonds in *trans*-$[CrR(acac)_2(H_2O)]$ complexes are cleaved heterolytically, the formation of *trans*-$[Cr(acac)_2(H_2O)_2]^+$ is expected as, at least, the immediate product.

Experimental Section

A. Preparation of Complexes. The complexes $[CrR(acac)_2(H_2O)]$[6,7] and $[Cr(acac)_3]$[8] were prepared as reported in the literature. The preparation of *cis*- and *trans*-$[Cr(acac)_2(H_2O)_2]X$ ($X = ClO_4^-, Cl^-$) were carried out by two methods: One is the literature method[4,5] with a slight modification (method 1); the other is the method developed in this work (method 2).

***cis*- and *trans*-$[Cr(acac)_2(H_2O)_2]ClO_4{\cdot}2H_2O$. Method 1.** $[Cr(acac)_3]$ (6.9 g, 20 mmol) was suspended in 200 mL of water at 90 °C. To the suspension was added a diluted aqueous perchloric acid solution (20 mmol) very slowly, and the pH of the solution was adjusted to be 2–4. Small amounts of ethanol were added repeatedly to increase the solubility of $[Cr(acac)_3]$. Water was also added repeatedly to maintain the original volume. Five days was needed to complete the reaction. After filtration, the final volume of the filtrate was adjusted to 50 mL. The solution was extracted with 50 mL of ether three times to remove $[Cr(acac)_3]$ and free Hacac. When the aqueous layer was evaporated to a small volume, the mixture of cis (violet) and trans (brown) isomers of $[Cr(acac)_2(H_2O)_2]ClO_4{\cdot}2H_2O$ crystallized simultaneously. The collected compounds were dissolved into a small volume of warm water. When the solution was cooled with an ice bath, the compounds deposited again. The cis and trans isomers were separated mechanically with slight difficulty, since the cis isomer is rather large grains but the trans isomer is fine crystals. Each compound was dried under vacuum. Total yield of both isomers: 2.9 g (35%). Anal. Calcd for $C_{10}H_{22}ClCrO_{12}$ ($[Cr(acac)_2(H_2O)_2]ClO_4{\cdot}2H_2O$): C, 28.48; H, 5.26. Found for violet crystals (cis isomer): C, 28.53; H, 4.94. Found for brown crystals (trans isomer): C, 28.17; H, 5.16.

Method 2. A solution of 50 mL of ethanol containing 2.7 g of $CrCl_3{\cdot}6H_2O$ (10 mmol), 2 g of 2,4-pentanedione (20 mmol), and 1 mL of concentrated HCl was stirred in the presence of 10 g of amalgamated zinc under a nitrogen atmosphere. The solution changed gradually from green to violet. After 3 h, the solution was filtered in air. Then, the filtrate was diluted with 300 mL of water. This solution was poured into a column (35 × 4.3 cm) containing SP-Sephadex C-25 resin (Na^+ form). The column showed three bands: violet, violet, and green species from the bottom to the top of the column. The lowest violet species was eluted with 0.1 M $NaClO_4$. When the eluent was evaporated to a small volume, white $NaClO_4$ deposited. After the salt was filtered, the filtrate was evaporated again. When the solution was cooled, both *cis*- (violet) and *trans*-$[Cr(acac)_2(H_2O)_2]ClO_4{\cdot}2H_2O$ (brown) crystallized simultaneously; total yield of both isomers 1.6 g (38%). The violet species of the middle band was identified as $[Cr(acac)(H_2O)_4]^{2+}$[2,3] from the measurement of its electronic spectrum.

When the elution was made with 0.1 M NaCl, *trans*-$[Cr(acac)_2(H_2O)_2]Cl{\cdot}H_2O$ was obtained exclusively.

***trans*-$[Cr(acac)_2(H_2O)_2]Cl{\cdot}H_2O$.** Dowex 1 resin ($Cl^-$ form; 3 mL) was added to a solution of *trans*-$[Cr(acac)_2(H_2O)_2]ClO_4{\cdot}2H_2O$ (0.5 g) in 10 mL of water. The suspension was filtered after stirring for a few minutes. The resin was washed with a small amount of water. The filtrate and the washing were combined and evaporated to a small volume. Brown crystals of *trans*-$[Cr(acac)_2(H_2O)_2]Cl{\cdot}H_2O$ deposited upon the addition of ethanol and then ether. The crystals were collected, washed with ether, and dried under vacuum. Anal. Calcd for $C_{10}H_{20}ClCrO_7$: C, 35.36; H, 5.93. Found: C, 35.42; H, 6.34.

Attempt To Prepare *cis*-$[Cr(acac)_2(H_2O)_2]Cl$. *cis*-$[Cr(acac)_2(H_2O)_2]ClO_4{\cdot}2H_2O$ was treated with Dowex 1 resin (Cl^- form) by a procedure similar to that for the preparation of *trans*-$[Cr(acac)_2(H_2O)_2]Cl{\cdot}H_2O$. However, *trans*-$[Cr(acac)_2(H_2O)_2]Cl{\cdot}H_2O$, instead of the cis isomer, gradually separated from the concentrated solution on long standing.

Optical Resolution of *cis*-$[Cr(acac)_2(H_2O)_2]ClO_4{\cdot}2H_2O$. *cis*-$[Cr(acac)_2(H_2O)_2]ClO_4{\cdot}2H_2O$ (1.0 g) was converted to an aqueous solution (total volume 10 mL) of *cis*-$[Cr(acac)_2(H_2O)_2]Cl$ by use of Dowex 1 resin (Cl^- form). To this solution was added a solution containing 1.2

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(1) Abbreviations used in this paper: Hacac, 2,4-pentanedione; en, ethylenediamine; H_4trdta, trimethylenediaminetetraacetic acid; H_2ox, oxalic acid.

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Table I. Electronic Spectral Data of $[Cr(acac)_2(H_2O)_2]^+$ in Aqueous Solutions

complex	λ_{max}/nm (log ϵ)	ref
cis isomer	553 (1.60), 388 (2.51), 328 (4.11), 257 (4.00)	this work
trans isomer[a]	527 (1.33), 384 (2.55), 328 (4.08), 263 (4.06)	this work
b	553 (1.59), 388 (2.55), 328 (4.15), 256 (3.96)	2, 3

[a] λ_{max} of solid $[Cr(acac)_2(H_2O)_2]Cl \cdot H_2O$ = 350 nm. [b] No description for the geometric configuration.

Table II. Acid Dissociation Constants of *cis*- and *trans*-$[Cr(acac)_2(H_2O)_2]^+$[a] and $[Cr(ox)_2(H_2O)_2]^-$[b]

		pK_1	pK_2
$[Cr(acac)_2(H_2O)_2]^+$	cis	7.06 ± 0.03	9.39 ± 0.03
	trans	6.89 ± 0.03	10.23 ± 0.03
$[Cr(ox)_2(H_2O)_2]^-$	cis	7.5	9.7
	trans	7.5	10.5

[a] T = 25.0 °C; I = 0.10 M. [b] T = 8 °C; I = 0.01 M. Values are from ref 12.

g of Δ-Ag[$(-)_{589}^{CD}$-Co(trdta)] in 10 mL of water.[9] After AgCl was removed by filtration, the filtrate was evaporated to 5 mL. Reddish violet crystals of $[(+)_{589}^{CD}\text{-}Cr(acac)_2(H_2O)_2][\Delta\text{-}Co(trdta)] \cdot 5.5H_2O$ appeared upon cooling the solution. The diastereoisomer was collected by filtration, and the filtrate was reserved for the isolation of $[(-)_{589}^{CD}\text{-}Cr(acac)_2(H_2O)_2]ClO_4 \cdot H_2O$. The diastereoisomer was recrystallized from water. Anal. Calcd for $C_{21}H_{43}CrCoN_2O_{19.5}$: C, 33.79; H, 5.81; N, 3.75. Found for $[Cr(acac)_2(H_2O)_2][Co(trdta)] \cdot 5.5H_2O$: C, 33.56; H, 6.17; N, 3.79. The diastereoisomer was converted by use of QAE-Sephadex resin (ClO_4^- form). When the solution was evaporated to a small volume by a rotary evaporator, $[(+)_{589}^{CD}\text{-}Cr(acac)_2(H_2O)_2]ClO_4 \cdot H_2O$ deposited. Anal. Calcd for $C_{10}H_{20}ClCrO_{11}$: C, 29.75; H, 4.99. Found: *cis*-$[Cr(acac)_2(H_2O)_2]ClO_4 \cdot H_2O$: C, 29.71; H, 5.38. $\Delta\epsilon_{549}$ = +0.63. This was not changed by recrystallization.

[Δ-Co(trdta)]$^-$ ions in the filtrate that had been reserved were exchanged with ClO_4^- ions by use of QAE-Sephadex resin (ClO_4^- form). When the solution was evaporated to a small volume, violet crystals of $[(-)_{589}^{CD}\text{-}Cr(acac)_2(H_2O)_2]ClO_4 \cdot H_2O$ deposited. $\Delta\epsilon_{549}$ = −0.61.

B. Spectral Measurements. Electronic spectra were recorded on Hitachi 330 and 100 and Shimazu UV-260 recording spectrophotometers, and circular dichroism (CD) spectra, on a Jasco J-40 spectrometer.

C. Determination of pK_a Values. For the determination of the pK_a values of *cis*- and *trans*-$[Cr(acac)_2(H_2O)_2]^+$, pH titrations were made with a standard sodium hydroxide solution under a nitrogen atmosphere at 25 °C and I = 0.1 M (NaCl). The titration curves were recorded on a Toa HSS-10A pH stat. The hydrogen ion concentrations were calculated with the activity coefficient of 0.83 for the hydrogen ion.[10]

Results and Discussion

Syntheses and Characterizations of *cis*- and *trans*-$[Cr(acac)_2(H_2O)_2]X \cdot nH_2O$ (X = ClO_4^-, Cl^-). In this work, violet and brown crystals of $[Cr(acac)_2(H_2O)_2]ClO_4 \cdot 2H_2O$ were obtained. The geometric structure of violet $[Cr(acac)_2(H_2O)_2]ClO_4 \cdot 2H_2O$ was proved to be cis unequivocally by resolution into its optical isomers. The brown crystals whose composition is the same as *cis*-$[Cr(acac)_2(H_2O)_2]ClO_4 \cdot 2H_2O$ must be the trans form. These assignments for the geometric structure were supported by the electronic spectral data and pK_a values.

The first ligand field band of *cis*-$[Cr(acac)_2(H_2O)_2]^+$ is located at a wavelength longer than that of the trans isomer as shown in Table I. The absorption coefficient of the first band of the cis complex is larger than that of the trans complex. The same tendency is observed for the pair *cis*-$[Cr(ox)_2(H_2O)_2]^-$ (λ_{max} = 562 nm; log ϵ = 1.71) and *trans*-$[Cr(ox)_2(H_2O)_2]^-$ (λ_{max} = 555 nm; log ϵ = 1.51).[11,12]

In Table II, the pK_a values of the cis and trans isomer pairs of $[Cr(acac)_2(H_2O)_2]^+$ and $[Cr(ox)_2(H_2O)_2]^-$ are compared. The pK_1 values of the cis and trans complexes of $[Cr(acac)_2(H_2O)_2]^+$ are quite similar to each other, but the pK_2 value of the trans isomer is much larger than that of the cis isomer. A similar tendency is also observed for the geometric isomers of $[Cr(ox)_2(H_2O)_2]^-$.[12] The phenomenon indicates that, in $[Cr(acac)_2(OH)(H_2O)]$ and $[Cr(ox)_2(OH)(H_2O)]^{2-}$ complexes, the electron donation from the hydroxo ligands makes the aqua ligands in the trans complexes more basic than those in the cis complexes.

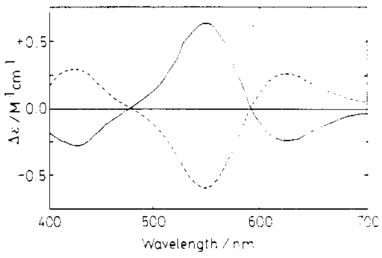
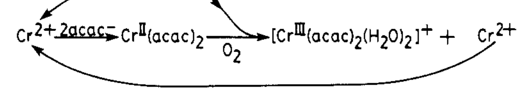


Figure 1. CD spectra of Λ- and Δ-*cis*-$[Cr(acac)_2(H_2O)_2]^+$ in aqueous solutions: (solid line) Λ isomer; (dotted line) Δ isomer.

Scheme I



Solid samples of *trans*-$[Cr(acac)_2(H_2O)_2]X \cdot nH_2O$ (X = ClO_4^-, Cl^-; n = 2 (ClO_4^-), 1 (Cl^-)) show a brown color. The band maximum of the solid sample of *trans*-$[Cr(acac)_2(H_2O)_2]Cl \cdot H_2O$ in a Nujol mull is located at 350 nm. However, when the solid sample is dissolved in water, the solution shows a violet color similar to that of the cis isomer. Therefore, the brown color of the trans complex in the solid state may be due to a specific crystal packing. For further elucidation of this phenomenon, the crystal structure analysis of a *trans*-$[Cr(acac)_2(H_2O)_2]X \cdot nH_2O$ crystal must be undertaken.

In Table I, the electronic spectral data for *cis*- and *trans*-$[Cr(acac)_2(H_2O)_2]^+$ are summarized. The spectral data reported by Balahura and Lewis[2,3] agree excellently with our data obtained for the cis isomer. Balahura and Lewis found that the reduction of $[Co(acac)_2(en)]^+$ by Cr^{2+} proceeds through an inner-sphere path involving both single-bridged and double-bridged transition states in addition to an outer-sphere path. They concluded that $[Cr(acac)_2(H_2O)_2]^+$ is produced via the double-bridged transition state. The result may imply that the inner-sphere reaction through the double-bridged transition state produces *cis*-$[Cr(acac)_2(H_2O)_2]^+$ exclusively.

The complete resolution of *cis*-$[Cr(acac)_2(H_2O)_2]^+$ was achieved easily by use of the optically active Ag[Co(trdta)]. Figure 1 shows the CD curve of $[(+)_{589}^{CD}\text{-}Cr(acac)_2(H_2O)_2]^+$, which was obtained from the diastereoisomer $[(+)_{589}^{CD}\text{-}Cr(acac)_2(H_2O)_2][\Delta\text{-}Co(trdta)] \cdot 5.5H_2O$. The CD spectrum of this isomer shows a negative and a positive peak from the longer wavelength of the first band and a negative peak under the second band. This implies that the complex ions have a Λ configuration. The CD pattern is very similar to that of Λ-$[(-)_{589}^{CD}\text{-}Cr(acac)_3]$,[13-15] whose chromophore is the same as that of *cis*-$[(+)_{589}^{CD}\text{-}Cr(acac)_2(H_2O)_2]^+$.

cis- and *trans*-$[Cr(acac)_2(H_2O)_2]X \cdot nH_2O$ were prepared by two methods. One is the method of Banerjea et al.[4,5] However, this method was found to be very time-consuming. In this work, a new synthetic procedure involving amalgamated zinc was invented. The reaction likely proceeds via the pathways shown in Scheme I. The product ratio of cis to trans isomer was found to be variable. When an aqueous solution containing *trans*-$[Cr(acac)_2(H_2O)_2]ClO_4 \cdot 2H_2O$ was evaporated to dryness very slowly

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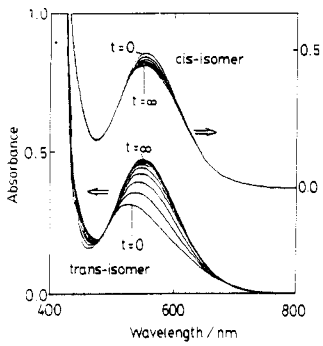

Figure 2. Spectral changes of *cis*- and *trans*-$[Cr(acac)_2(H_2O)_2]^+$ complexes in aqueous solutions at 45 °C. Time intervals are 1 h. [cis isomer]$_0$ = 1.22×10^{-2} M; [trans isomer]$_0$ = 1.33×10^{-2} M.

Table III. Equilibrium Constants (K) and Rate Constants (k_f and k_b) of Isomerization Reactions of *cis*- and *trans*-$[Cr(acac)_2(H_2O)_2]^+$ Ions[a]

	temp/°C		
	35	45	53
K^b	7.7 ± 0.5	7.1 ± 0.4	6.7 ± 0.4
$k_f/10^{-4}\ s^{-1}$	0.18 ± 0.01		2.3 ± 0.1
$k_b/10^{-4}\ s^{-1}$	0.024 ± 0.003		0.34 ± 0.04

[a] No indifferent salt was added. [b] $\Delta H° = -7 \pm 3$ kJ mol^{-1}, $\Delta S° = -4 \pm 9$ J K^{-1} mol^{-1}.

over concentrated sulfuric acid in a desiccator, only the cis isomer deposited. Both isomers interconvert in aqueous solutions, as will be mentioned below. The chloride salt solution of $[Cr(acac)_2(H_2O)_2]^+$ gave crystals of the trans isomer (see Experimental Section). Therefore, the yields of cis and trans isomers depend on the solubility of the isomers, the ease of crystallization, and the time required for the evaporation of the solvent.

Cis–Trans Isomerization of $[Cr(acac)_2(H_2O)_2]^+$. When *trans*-$[Cr(acac)_2(H_2O)_2]ClO_4 \cdot 2H_2O$ is dissolved in water, the absorption peak of the first band shifts to longer wavelength with time (see Figure 2). On the other hand, the absorption peak of the cis isomer shifts to shorter wavelength with time and the final spectrum coincides with that of the trans isomer. This implies that each of the *cis*- and *trans*-$[Cr(acac)_2(H_2O)_2]^+$ complexes isomerizes to give an equilibrium mixture of *cis*- and *trans*-$[Cr(acac)_2(H_2O)_2]^+$ complexes:

$$trans\text{-}[Cr(acac)_2(H_2O)_2]^+ \underset{k_b}{\overset{k_f}{\rightleftharpoons}} cis\text{-}[Cr(acac)_2(H_2O)_2]^+ \quad (1)$$

The equilibrium constant, K, defined by eq 2 was calculated from the absorbance (A) of an equilibrated solution at a given wavelength and the total chromium concentration ($[Cr]_T$ = [trans isomer] + [cis isomer]) by use of eq 3, where ϵ_C and ϵ_T denote

$$K = \frac{[\text{cis isomer}]}{[\text{trans isomer}]} \quad (2)$$

$$K = \frac{A - \epsilon_T[Cr]_T}{\epsilon_C[Cr]_T - A} \quad (3)$$

the molecular extinction coefficients of the cis and trans isomers at the given wavelength, respectively. The equilibrium constants determined at various temperatures and the thermodynamic parameters are given in Table III.

The kinetics of the cis–trans isomerization reactions were carried out. The reaction followed the first-order rate law. The observed first-order rate constant (k_{obsd}) must correspond to the sum of the k_f and k_b values given in eq 1, because reaction 1 is reversible. The k_f and k_b values were calculated by the equations

$$k_f = \frac{K}{K+1}k_{obsd} \quad (4)$$

$$k_b = \frac{1}{K+1}k_{obsd} \quad (5)$$

The values determined are given in Table III.

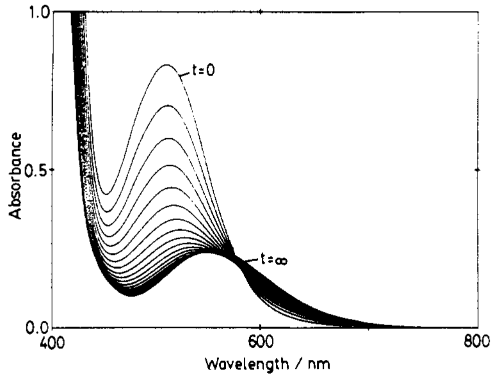

Figure 3. Spectral changes of 8.1×10^{-3} M $[Cr(CHCl_2)(acac)_2(H_2O)]$ in an aqueous solution at 35 °C. Time intervals are 90 min.

Reactions of $[CrR(acac)_2(H_2O)]$ (R = $CHCl_2$, CH_2Cl) in Aqueous Solutions. Figure 3 shows the spectral changes of $[Cr(CHCl_2)(acac)_2(H_2O)]$ in an aqueous solution with time. Spectral changes similar to this were also observed for $[Cr(CH_2Cl)(acac)_2(H_2O)]$. The pH of the solution after the reaction was found to be 3.81 for R = $CHCl_2$ ([complex] = 2.81×10^{-3} M) and 4.96 for R = CH_2Cl ([complex] = 2.80×10^{-3} M), respectively. It is seen in Figure 3 that the reaction occurs in at least two steps. At the first step of the reaction, an isosbestic point is observed at 580 nm. The absorption maximum at 507 nm, which is characteristic of the complexes containing a chromium–carbon bond,[16–18] disappears with time. The absorption maximum of the final spectrum at the first step of the reaction is observed at around 550 nm. Then, the isosbestic point at 580 nm begins to collapse and the absorption maximum shifts further to the longer wavelength. The final absorption maximum is positioned at around 555 nm.

First of all, we attempted to explain these spectral changes as the occurrence of the two consecutive reactions

first step

$$trans\text{-}[CrR(acac)_2(H_2O)] \xrightarrow{k_1} trans\text{-}[Cr(acac)_2(H_2O)_2]^+ + \text{products derived from the R group} \quad (6)$$

second step

$$trans\text{-}[Cr(acac)_2(H_2O)_2]^+ \underset{k_b}{\overset{k_f}{\rightleftharpoons}} cis\text{-}[Cr(acac)_2(H_2O)_2]^+ \quad (7)$$

If this is the case, the differential rate equations for reactions 6 and 7 can be expressed as

$$-\frac{d[R]}{dt} = k_1[R] \quad (8)$$

$$\frac{d[T]}{dt} = k_1[R] - k_f[T] + k_b[C] \quad (9)$$

$$\frac{d[C]}{dt} = k_f[T] - k_b[C] \quad (10)$$

where R, T, and C denote *trans*-$[CrR(acac)_2(H_2O)]$, *trans*-$[Cr(acac)_2(H_2O)_2]^+$, and *cis*-$[Cr(acac)_2(H_2O)_2]^+$, respectively. The solutions are[19]

$$[R] = [R]_0 \exp(-k_1 t) \quad (11)$$

$$[T] = [R]_0 - [R] - [C] \quad (12)$$

$$[C] = [R]_0 k_f\left(\frac{1}{k_f + k_b} + \frac{1}{k_1 - k_f - k_b}\exp(-k_1 t) - \frac{k_1}{(k_f + k_b)(k_1 - k_f - k_b)}\exp[-(k_f + k_b)t]\right) \quad (13)$$

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Table IV. Kinetic Data for the Chromium–Carbon Bond-Cleavage Reactions of $[CrR(acac)_2(H_2O)]$ (R = $CHCl_2$, CH_2Cl) in Aqueous Solutions

R	temp/°C	I ($LiClO_4$)/M	$k_1/10^{-4}$ s^{-1}
$CHCl_2$	35	*a*	0.45 ± 0.03
	53	*a*	3.8 ± 0.2
	53	0.1	3.9 ± 0.2
CH_2Cl	53	0.1	3.2 ± 0.2

[a] No indifferent salt was added.

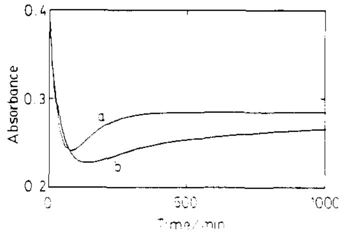

Figure 4. Calculated (curve a) and observed (curve b) absorbance changes of 8.0×10^{-3} M $[Cr(CHCl_2)(acac)_2(H_2O)]$ in an aqueous solution at 564 nm and 53 °C.

where $[R]_0$ denotes the initial concentration of *trans*-$[CrR(acac)_2(H_2O)]$. The absorbance at a given time can be expressed as

$$A = A_\infty + \alpha \exp(-k_1 t) + \beta \exp[-(k_f + k_b)t] \qquad (14)$$

$$A_\infty = \frac{k_f \epsilon_C + k_b \epsilon_T}{k_f + k_b}[R]_0$$

$$\alpha = \frac{(k_1 - k_b)(\epsilon_R - \epsilon_T) - k_f(\epsilon_R - \epsilon_C)}{k_1 - k_f - k_b}[R]_0$$

$$\beta = \frac{k_1 k_f(\epsilon_T - \epsilon_C)}{(k_f + k_b)(k_1 - k_f - k_b)}[R]_0$$

where the subscripts 0 and ∞ denote $t = 0$ and infinity, respectively.

When $\epsilon_T = \epsilon_C$, eq 14 is simplified as

$$A = A_\infty + (\epsilon_R - \epsilon_T)[R]_0 \exp(-k_1 t) \qquad (15)$$

When the reaction was followed at 490 nm, where the absorbance change due to the second step of the reaction is minimal, plots of ln ($A - A_\infty$) vs time gave a linear relation for 3 half-lives. The k_1 values thus obtained are listed in Table IV.

In contrast to our expectation, it was disclosed that the spectral changes shown in Figure 3 cannot be explained by considering only the occurrence of reactions 6 and 7. Figure 4 shows the absorbance change with time observed for $[Cr(CHCl_2)(acac)_2(H_2O)]$ at 564 nm. The calculated line is also shown in Figure 4 by use of eq 14 since all numerical data in eq 14 have been determined in this work. The observed rate of the absorbance increase that was considered to correspond to reaction 7 is much smaller than the calculated one. A similar discrepancy between the observed and calculated curves is also found for $[Cr(CH_2Cl)(acac)_2(H_2O)]$. In Figure 5, the final spectrum shown in Figure 3 is compared with the spectra of the equilibrium mixture of *cis*- and *trans*-$[Cr(acac)_2(H_2O)_2]^+$ and $[Cr(acac)(H_2O)_4]^{2+}$. The final spectrum lies between the spectra of the equilibrium mixture of *cis*- and *trans*-$[Cr(acac)_2(H_2O)_2]^+$ and $[Cr(acac)(H_2O)_4]^{2+}$. This suggests that formation of $[Cr(acac)(H_2O)_4]^{2+}$ as well as reactions 6 and 7 contributes to the spectral changes observed in Figure 3.

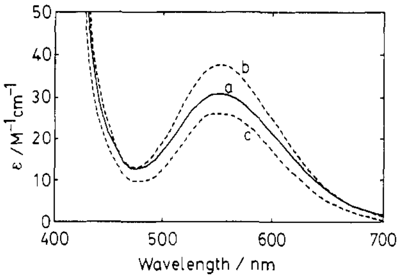

Figure 5. Comparison of the final spectrum shown in Figure 3 (curve a) with the spectra of the equilibrium mixture of *cis*- and *trans*-$[Cr(acac)_2(H_2O)_2]^+$ (curve b, measured at 35 °C) and $[Cr(acac)(H_2O)_4]^{2+}$ (curve c).

Spreer et al. investigated the cleavage reactions of the chromium–carbon bond in $[Cr(CHX_2)(H_2O)_5]^{2+}$ (X = Cl, Br, I).[20] The final products of the reaction were identified as Cr^{3+}, CO, H_2, and formic acid. From the result and kinetics of the reaction, they proposed a mechanism in which a chromium–formyl intermediate, $CrCHO^{2+}$, is formed. In this work, a preliminary experiment was carried out for surveying product(s) derived from the $CHCl_2$ group in $[Cr(CHCl_2)(acac)_2(H_2O)]$: When $[Cr(CHCl_2)(acac)_2(H_2O)]$ was dissolved in pure water and heated at 60 °C for 9 h, gases evolved. The amount of the gaseous products (0.123 mmol) was approximately half of that of the initial complex (0.266 mmol). One of the gaseous products was identified as carbon monoxide by a gas-phase infrared spectral measurement. Therefore, this suggests that the chromium–carbon bond-cleavage reaction of $[Cr(CHCl_2)(acac)_2(H_2O)]$ proceeds through the formation of a chromium–formyl intermediate, $[Cr(CHO)(acac)_2(H_2O)]$. Further mechanistic studies are still being carried out.

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