largest ionic M^{III} radius in the first transition series.

Kinetic Features of $Sc^{III}O_6$ Complexes. The k_1 defined above is calculated to be 80 s^{-1} at 25 °C by extrapolation of [enol] for the present exchange. The LFER shows that the first-order rate constant, $k_1(H_2O)$, of water exchange and anation of $[M^{III}L_5(H_2O)]^{3+}$ (L = H_2O and/or NH_3) are larger than k_1 by about 10^4–10^5 invariably for various M^{III}.[7] The relationship and the present data indicate that $k_1(H_2O)$ for $[Sc^{III}(H_2O)_6]^{3+}$, if it exists, is most probably 10^6–10^7 s^{-1}, although the hydration number of the ion is still uncertain in spite of a recent X-ray diffraction study on aqueous solutions of $ScCl_3$ and $Sc(ClO_4)_3$ (frequency factor of Sc–O 6–8).[14]

It is pointed out that the Sc^{III} complexes such as $[ScF_6]^{3-}$, $[Sc(bpy)_3]^{3+}$, $[ScCl_2(bpy)_2]^+$ (bpy = 2,2′-bipyridine), $[Sc(DMSO)_6]^{3+}$ (DMSO = dimethyl sulfoxide) exhibit the usual coordination number of 6 and that Sc^{III} has a greater similarity to Al^{III} rather than to Y^{III}, La^{III}, and tervalent lanthanides in the physical properties of $Na_3M^{III}F_6$ crystals and in the stability constant of ethylenediaminetetraacetate complexes in aqueous solution.[15,16] In the present exchange, Sc^{III} shows a remarkable similarity to In^{III} rather than Al^{III} in the ΔH^* and ΔS^* values (Table IV); hence, the k_1' ratio of Sc^{III} to In^{III} at 25 °C is only 50. The same tendency has been found in the ligand exchange of $[Sc(TMP)_6]^{3+}$ and $[In^{III}(TMP)_6]^{3+}$ in nitromethane, where ΔH^*/kJ mol^{-1}, ΔS^*/J K^{-1} mol^{-1}, and ΔV^*/cm^3 mol^{-1} values are 21.2, −144, and −18.7 for Sc^{III} and 32.8, −118, and −22.8 for In^{III}, respectively, and the corresponding ratio of the second-order rate constants is 5.[5b,c] For $[Al^{III}(TMP)_6]^{3+}$, quite different values of the activation parameters were reported (85.1, +38.2, and +22.5, respectively).[5b,c] Therefore, as for the ligand substitution behavior, $Sc^{III}O_6$ is concluded to be akin to $In^{III}O_6$ rather than $Al^{III}O_6$. Any similar transition metal $M^{III}(acac)_3$ could not be found in the present exchange (Table IV). The similarity is attributed mainly to the ionic radius (Table IV), which dominates electrostatic interactions between M^{III} and the ligand in the substitution process, since the ions have d^0 or d^{10} configurations and are hence unaffected by ligand field change in the activation process.

In conclusion, $Sc^{III}O_6$ complexes seem to have generally similar features in the ligand substitution process to $In^{III}O_6$ features in both lability and mechanism because of steric and electronic features of the central metal ions.

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Registry No. $Sc(acac)_3$, 14284-94-7; Hacac, 17272-66-1; D_2, 7782-39-0.

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Volume Profile for Aquations of the (Carboxylato)pentaamminecobalt(III) Complex

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The activation volume (ΔV^*) and reaction volume (ΔV) have been experimentally obtained for nine reactions of the title complex. ΔV ranges from −14 to −18 cm^3 mol^{-1} for the carboxylato leaving ligand and from −3 to −6 cm^3 mol^{-1} for the carboxylic acid leaving ligand. ΔV^* is approximately half of the corresponding ΔV. This feature supports an interchange mechanism for these reactions.

Introduction

Volume profiles for aquations of anionopentaamminecobalt(III)

$$Co(NH_3)_5X^{n+} + H_2O = Co(NH_3)_5H_2O^{3+} + X \qquad (1)$$

were investigated previously for X = Cl^-, Br^-, NO_3^-, SO_4^{2-}, Me_2SO, H_2O, $OHCH_3$, $OHCH_2CH_3$, $OHCH(CH_3)_2$, $OC(NH_2)_2$, $OC(NH_2)(NHCH_3)$, $OC(NHCH_3)_2$, $OCH(NH_2)$, $OCH(NHCH_3)$, and $OCH(N(CH_3)_2)$.[2-5] It was suggested that the correlation

$$\Delta V^* = (0.51 \pm 0.02)\Delta V + (1.2 \pm 0.2) \qquad (2)$$

exists between their ΔV^* and ΔV values.[6] Equation 2 means that the partial molal volume ($\bar{V}$) of the transition state is close to the corresponding mean $\bar{V}$ of the initial and the final state. It was interpreted that the entering H_2O and the leaving X participate almost equally in the transition state, and an interchange mechanism was supported. In the present work, we intend to check the applicability of eq 2 to the extended series of reaction 1 with carboxylato and carboxylic acid leaving ligands.

In previous work at normal pressure, it was shown that the aquation velocity of $Co(NH_3)_5(RCOO)^{2+}$ (R = H, CH_3, C_2H_5, $CHCl_2$, CH_2Cl, and CCl_3) depends more or less on the acidity of the solution.[7,8] This dependence was remarkable when the corresponding RCOOH was weak acid. In the case of R = H and C_2H_5, the aquation rate constant k_{obsd} depends linearly on $[H^+]$:[8]

$$k_{obsd} = k_0 + k_1[H^+] \qquad (3)$$

Thus, it was considered that the reaction proceeds through two paths:[8]

k_0 path

$$Co(NH_3)_5(RCOO)^{2+} + H_2O \xrightarrow{k_0} Co(NH_3)_5H_2O^{3+} + RCOO^- \qquad (4)$$

k_1 path

$$Co(NH_3)_5(RCOO)^{2+} + H^+ \overset{K}{\rightleftharpoons} Co(NH_3)_5(RCOOH)^{3+} \qquad (5)$$

$$Co(NH_3)_5(RCOOH)^{3+} + H_2O \xrightarrow{k_H} Co(NH_3)_5H_2O^{3+} + RCOOH \qquad (6)$$

$$RCOOH \overset{K_a}{\rightleftharpoons} RCOO^- + H^+ \qquad (7)$$

$$k_1 = Kk_H$$

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Table I. Aquation Rate of $Co(NH_3)_5(RCOO)^{2+}$ at Normal Pressure and an Ionic Strength (μ) of 0.4 M ($NaClO_4$)

	$[HClO_4]$/ M	10^5k_{obsd}/ s^{-1}
R = CH_2Br, $[Co^{III}]^a$ = 0.001 M, t = 75 °C,	0.10	2.37
λ = 274 nm,^{b} $k_0 = 0.77 \times 10^{-5}\ s^{-1}$,	0.25	4.85
$k_1 = 16.2 \times 10^{-5}\ M^{-1}\ s^{-1}$	0.40	7.23
R = $CHBr_2$, $[Co^{III}]^a$ = 0.001 M, t = 80 °C,	0.01	3.73
λ = 274 nm,^{b} $k_0 = 3.7 \times 10^{-5}\ s^{-1}$,	0.20	3.83
$k_1 = 1.42 \times 10^{-5}\ M^{-1}\ s^{-1}$	0.40	4.28
R = CF_3, $[Co^{III}]^a$ = 0.0003 M, t = 75 °C,	0.01	10.4
λ = 244 nm^b	0.20	10.7
	0.40	10.6

^{a}Concentration of the complex. ^{b}Reaction was followed at this wavelength.

It was suggested that when RCOOH is a weak acid, the K value is relatively large and the $k_1[H^+]$ term predominates in eq 3.

In the present work, it has been found that k_{obsd} at normal pressure also satisfies eq 3 in the case of R = CH_2Br and $CHBr_2$ and that k_{obsd} is independent of $[H^+]$ in the case of R = CF_3. Thus, we assume eq 3 throughout the series of $Co(NH_3)_5(RCOO)^{2+}$. In the case of R = H, CH_3, C_2H_5, CH_2Cl, and CH_2Br, the pressure dependence of k_{obsd} has been investigated at $[HClO_4]$ = 0.4 M, where the contribution of the k_0 path is negligible (M = mol dm^{-3}). The activation volume for the k_1 path is obtained from

$$\Delta V^{*}_1 = -RT\frac{d \ln k_1}{dP} = -RT\frac{d \ln k_{obsd}}{dP} \tag{8}$$

Therefrom

$$\Delta V^{*}_H = -RT\frac{d \ln k_H}{dP} = \Delta V^{*}_1 - \Delta V(5) \tag{9}$$

is calculated.[9] In the case of R = $CHCl_2$, $CHBr_2$, CCl_3, and CF_3, the pressure dependence of k_{obsd} has been investigated at $[HClO_4]$ = 0.01 M and $[NaClO_4]$ = 0.39 M, where the contribution of the k_1 path is negligible. The activation volume for the k_0 path is calculated by

$$\Delta V^{*}_0 = -RT\frac{d \ln k_0}{dP} = -RT\frac{d \ln k_{obsd}}{dP} \tag{10}$$

The partial molal volumes at infinite dilution ($\bar{V}^{\circ}$) of the complex and the leaving ligand have been determined by densimetry, and ΔV for aquation has been calculated.

Experimental Section

The complexes $[Co(NH_3)_5(HCOO)](ClO_4)_2$, $[Co(NH_3)_5(CH_3COO)](ClO_4)_2$, $[Co(NH_3)_5(C_2H_5COO)](ClO_4)_2$, $[Co(NH_3)_5(C_2H_5COO)](ClO_4)_2 \cdot 2.5H_2O$, $[Co(NH_3)_5(CH_2ClCOO)](ClO_4)_2$, $[Co(NH_3)_5(CHCl_2COO)](ClO_4)_2$, $[Co(NH_3)_5(CCl_3COO)](ClO_4)_2$, and $[Co(NH_3)_5(CF_3COO)](ClO_4)_2$ were obtained by adding concentrated $HClO_4$ to an aqueous solution of the corresponding nitrate.[10] The complexes $[Co(NH_3)_5(CH_2ClCOO)](NO_3)_2$, $[Co(NH_3)_5(CH_2BrCOO)](ClO_4)_2$, $[Co(NH_3)_5(CHBr_2COO)](ClO_4)_2$, and $[Co(NH_3)_5H_2O](ClO_4)_3$ were obtained according to published methods.[10-12] All these complexes were identified by elemental analysis (CHN). Their UV-vis absorption spectra coincided well with the published ones.[8,11,13] Nakarai GR or EP grade chemicals were used without further purification.

Kinetics at high pressure were carried out as before by using a thermostated (±0.1 °C) high-pressure apparatus capable of removal of several aliquots.[14] The reaction was followed by UV absorption. Densimetry and dilatometry were carried out as before at 25 ± 0.001 °C.[15,16]

Results

Kinetic Results at Normal Pressure. These results are summarized in Table I. For R = CH_2Br and $CHBr_2$, k_{obsd} depends linearly on $[H^+]$. For R = CF_3, k_{obsd} is independent of $[H^+]$. This tendency is quite in line with previous observations.[8] The dependence on $[H^+]$ is more remarkable when the corresponding carboxylic acid is weaker: $pK_a(CH_2BrCOOH)$ (=2.90) > $pK_a(CHBr_2COOH)$ (=1.53) > $pK_a(CF_3COOH)$.

Kinetic Results at High Pressure. Values of k_{obsd} at high pressure are summarized in Table II. In all cases, k_{obsd} increases slightly with an increase of the pressure and negative values of ΔV^{*}_1 or ΔV^{*}_0 can be obtained by eq 8 or 10.

Densimetric Results. The density of the aqueous solution of $Co(NH_3)_5(RCOO)^{2+}$ was measured at four concentrations of the complex (0.01–0.04 M). The resulting apparent molal volumes ϕ_v(obsd) were essentially independent of the concentration. $\bar{V}^{\circ}$ is obtained as the mean value of $\phi_v(obsd) - 9.706c^{1/2}$, where c is the molar concentration.[15] The density of the $[Co(NH_3)_5H_2O](ClO_4)_3$ solution was measured at five concentrations (0.01–0.05 M). ϕ_v(obsd) increased slightly with increasing c. $\bar{V}^{\circ}$ is obtained as the intercept of the $\phi_v(obsd) - 27.453c^{1/2}$ against c plot with a gradient of -40.2×10^3 cm^6 mol^{-2}. the densities of the aqueous solutions of $CH_2ClCOONa$, $CHCl_2COONa$, CCl_3COONa, and CF_3COONa were measured at five concentrations (0.02–0.1 M). ϕ_v(obsd) increased very slightly with an increase of c. $\bar{V}^{\circ}$ is obtained as the mean value of $\phi_v(obsd) - 1.868c^{1/2}$.[15] The densities of the aqueous solutions of $CH_2BrCOOH$ and $CHBr_2COOH$ were measured at nine concentrations (0.01–0.10 M). ϕ_v(obsd) increased with an increase of c. In this case, it was assumed as

$$\phi_v(obsd) = (1 - \alpha)\phi_{HA} + \alpha\phi_{H^+A^-} \tag{11}$$

$$\phi_{HA} = \bar{V}^{\circ}_{HA} + hc_{HA} \tag{12}$$

$$\phi_{H^+A^-} = \bar{V}^{\circ}_{H^+A^-} + 1.868c_{H^+A^-}{}^{1/2} \tag{13}$$

$$c_{HA} = (1 - \alpha)c \tag{14}$$

$$c_{H^+A^-} = \alpha c \tag{15}$$

where α is the degree of the acidic dissociation and h is a constant. The $\bar{V}^{\circ}_{HA}$ etc. values denote the $\bar{V}^{\circ}$ value of the acid HA etc. From eq 11–15

$$\phi_v(obsd) - \alpha(\bar{V}^{\circ}_{H^+A^-} - \bar{V}^{\circ}_{HA}) - 1.868\dot{\alpha}(\alpha c)^{1/2} = \bar{V}^{\circ}_{HA} + h(1 - \alpha)^2c \tag{16}$$

was derived. The left side of eq 16 was calculated at each concentration, where α was estimated from the titmetrically determined thermodynamic pK_a = 2.90 for $CH_2BrCOOH$ and pK_a = 1.53 for $CHBr_2COOH$. In the case of $CH_2BrCOOH$, dilatometrically obtained $\Delta V(7) = \bar{V}^{\circ}_{H^+A^-} - \bar{V}^{\circ}_{HA} = -9.0$ cm^3 mol^{-1} was used. In the case of $CHBr_2COOH$, assuming as $\Delta V(7) = -8.9$ cm^3 mol^{-1}, the best linear correlation was obtained between the left side of eq 16 and $(1 - \alpha)^2c$. $\bar{V}^{\circ}_{HA}$ is obtained as the intercept of this plot. The results are summarized in Table III.

Calculation of ΔV^{*} and ΔV. In a previous work, ΔV values were measured for a series of reactions:

$$MA^z + OH^- = MB^{z-1} + H_2O$$

where MA^z is an octahedral transition-metal complex with ligand A = OH_2, NH_3, $C_2O_4H^-$ and MB^{z-1} is the corresponding conjugate base complex with ligand B = OH^-, NH_2^-, $C_2O_4^{2-}$.[16] The results were expressed as

$$\Delta V\ (cm^3\ mol^{-1}) = (14.5 \pm 0.8) - (2.5 \pm 0.2)\Delta Z^2 \tag{17}$$

where $\Delta Z^2 = (z - 1)^2 - z^2$. According to eq 17, we estimate $\Delta V(5) = -4.9$ cm^3 mol^{-1} throughout the series of $Co(NH_3)_5(RCOO)^{2+}$ complexes, where $\Delta V = -22.1$ cm^3 mol^{-1} for $H_2O = H^+ + OH^-$ is used.[16] Then, ΔV^{*}_H can be obtained from ΔV^{*}_1 in Table II

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(9) In this report, $\Delta V(5)$ etc. denote the ΔV values of reaction 5 etc.

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Table II. Pressure Dependence of the Rates and the Activation Volumes for Aquation of $Co(NH_3)_5(RCOO)^{2+}$ at $\mu = 0.4$ M ($NaClO_4$)

R	H	CH_3	C_2H_5	CH_2Cl	CH_2Br
$[Co^{III}]$/M[a]	0.001	0.001	0.001[d]	0.001	0.001
t/°C[b]	64.5	64.5	64.5	74.5	74.5
λ/nm[c]	270	270	280	270	274
$[HClO_4]$/M	0.4	0.4	0.4	0.4	0.4
$\Delta V^{\ddagger}_1$/cm³ mol⁻¹	−5.8 ± 0.3	−4.2 ± 0.3	−4.4 ± 0.4	−4.5 ± 0.4	−6.4 ± 0.3

	$10^5k_{obsd}/s^{-1}$									
P/MPa	R = H		R = CH_3		R = C_2H_5		R = CH_2Cl		R = CH_2Br	
5	15.3	15.1	27.0	26.7	20.8	22.4	5.95	6.19	6.73	6.71
50	17.2	17.3	29.9	29.7	23.9	23.1	6.59	6.74	7.75	7.56
100	19.6	18.8	31.8	31.5	26.1	24.9	6.86	7.26	8.46	8.76
150	21.0	20.4	35.4	33.5	28.1	27.4	7.72	8.04	9.89	9.34
200	23.2	22.9	36.5	35.6	28.4	29.8	8.36	8.09	10.3	10.4

R	$CHCl_2$	$CHBr_2$	CCl_3	CF_3
$[Co^{III}]$/M[a]	0.001	0.001	0.001	0.0003
t/°C[b]	79.5	79.5	74.5	74.5
λ/nm[c]	270	274	264	252
$[HClO_4]$/M	0.01	0.01	0.01	0.01
$\Delta V^{\ddagger}_0$/cm³ mol⁻¹	−7.0 ± 0.3	−6.4 ± 0.2	−5.7 ± 0.4	−5.7 ± 0.3

	$10^5k_{obsd}/s^{-1}$							
P/MPa	R = $CHCl_2$		R = $CHBr_2$		R = CCl_3		R = CF_3	
5	3.98	4.05	3.42	3.41	8.51	8.95	8.52	8.76
50	4.33	4.64	3.76	3.82	9.77	10.2	9.04	9.53
100	5.21	4.89	4.26	4.20	10.7	11.2	10.8	10.4
150	5.64	5.64	4.88	4.68	11.5	11.5	11.2	11.4
200	6.40	6.46	5.11	5.30	13.1	13.2	12.9	12.5

[a] Concentration of the complex perchlorate. [b] Reaction temperature. [c] Reaction was followed at this wavelength. [d] The 2.5-water solvate was used.

Table III. Values of Partial Molal Volumes Obtained in This Work at 25 °C

solute	$\bar{V}^\circ$/ cm³ mol⁻¹	$\bar{V}^\circ_{cation}$/ cm³ mol⁻¹	$\bar{V}^\circ_{anion}$/ cm³ mol⁻¹
$[Co(NH_3)_5(HCOO)](ClO_4)_2$	184.3	85.3	49.5[a]
$[Co(NH_3)_5(CH_3COO)](ClO_4)_2$	202.4	103.4	49.5[a]
$[Co(NH_3)_5(C_2H_5COO)](ClO_4)_2$[b]	218.8	119.8	49.5[a]
$[Co(NH_3)_5(CF_3COO)](ClO_4)_2$	213.4	114.4	49.5[a]
$[Co(NH_3)_5(CH_2ClCOO)](NO_3)_2$	182.5	113.7	34.4[a]
$[Co(NH_3)_5(CHCl_2COO)](ClO_4)_2$	225.8	126.8	49.5[a]
$[Co(NH_3)_5(CCl_3COO)](ClO_4)_2$	239.9	140.9	49.5[a]
$[Co(NH_3)_5(CH_2BrCOO)](ClO_4)_2$	216.8	117.8	49.5[a]
$[Co(NH_3)_5(CHBr_2COO)](ClO_4)_2$	234.6	135.6	49.5[a]
$[Co(NH_3)_5H_2O](ClO_4)_3$	203.2	54.7	49.5[a]
$CH_2ClCOONa$	50.2	−6.6[a]	56.8
$CHCl_2COONa$	65.1	−6.6[a]	71.7
CCl_3COONa	79.6	−6.6[a]	86.2
CF_3COONa	56.8	−6.6[a]	63.4
$CHBr_2COOH$	86.2	−5.4[a]	82.7
$CH_2BrCOOH$	66.5	−5.4[a]	62.9

[a] Reference 17. [b] Anhydrate was used.

Table IV. ΔV° for the Acidic Dissociation and $\bar{V}^\circ$ of the Anion at 25 °C

acid	ΔV°/cm³ mol⁻¹	$\bar{V}^\circ_{anion}$/cm³ mol⁻¹
HCOOH	−8.5[a]	31.7[c]
CH_3COOH	−11.3[a]	45.9[c]
C_2H_5COOH	−13.0[a]	59.4[c]
$CH_2ClCOOH$	−8.5[b]	
$CH_2BrCOOH$	−9.0[b]	
$CHBr_2COOH$	−8.9[b]	

[a] Reference 18. [b] This work. [c] Reference 17.

according to eq 9. $\Delta V(4)$ is calculated from the $\bar{V}^\circ$ values in Tables III and IV.

$$\Delta V(4) = \bar{V}^\circ(Co(NH_3)_5H_2O^{3+}) + \bar{V}^\circ(RCOO^-) - \bar{V}^\circ(Co(NH_3)_5(RCOO)^{2+}) - \bar{V}^\circ(H_2O)$$

$\Delta V(6)$ is calculated by

$$\Delta V(6) = \Delta V(4) - \Delta V(5) - \Delta V(7)$$

where $\Delta V(7)$ in Table IV is used. The results are summarized in Table V.

Table V. Values of $\Delta V^{\ddagger}$ and ΔV for the Aquation of $Co(NH_3)_5(RCOO)^{2+}$ and $Co(NH_3)_5(RCOOH)^{3+}$

leaving ligand	$\Delta V^{\ddagger}$/ cm³ mol⁻¹	ΔV/ cm³ mol⁻¹	leaving ligand	$\Delta V^{\ddagger}$/ cm³ mol⁻¹	ΔV/ cm³ mol⁻¹
HCOOH	−0.9	−3.6	$CHCl_2COO^-$	−7.0	−18.5
CH_3COOH	0.7	−4.7	$CHBr_2COO^-$	−6.4	−16.3
C_2H_5COOH	0.5	−5.9	CCl_3COO^-	−5.7	−18.1
$CH_2ClCOOH$	0.4	−6.9	CF_3COO^-	−5.7	−14.4
$CH_2BrCOOH$	−1.5	−4.4			

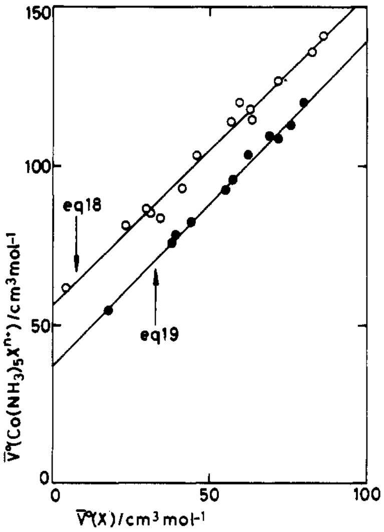

Figure 1. Correlation between $\bar{V}^\circ(Co(NH_3)_5X^{n+})$ and $\bar{V}^\circ(X)$: (○) X with −1 charge; (●) neutral X. Data are taken from this work and ref 5.

Discussion

As illustrated in Figure 1, a good linear correlation exists between the $\bar{V}^\circ$ values of $Co(NH_3)_5X^{2+}$ and X^-, where X^- includes F^-, Cl^-, Br^-, I^-, NO_3^-, and 9 $RCOO^-$ species:

$$\bar{V}^\circ(Co(NH_3)_5X^{2+}) = (0.98 \pm 0.04)[\bar{V}^\circ(X^-)] + (56.2 \pm 2.1) \quad (18)$$

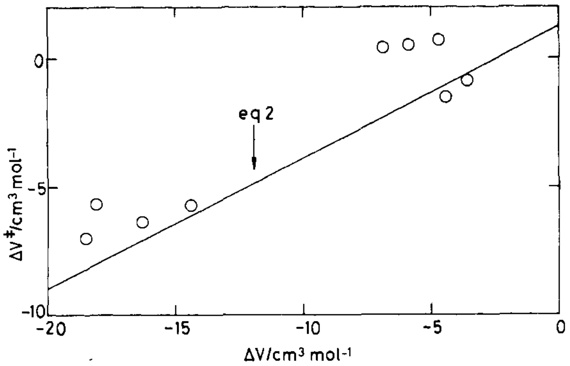

Figure 2. Correlation between $\Delta V^\ddagger$ and ΔV for the aquation of $Co(NH_3)_5(RCOO)^{2+}$ and $Co(NH_3)_5(RCOOH)^{3+}$.

This is quite analogous to the correlation pointed out by Lawrance in the case of 11 neutral ligands X^0:[5]

$$\bar{V}^\circ(Co(NH_3)_5X^{3+}) = (1.0 \pm 0.03)[\bar{V}^\circ(X^0)] + (37.0 \pm 1.6) \quad (19)$$

These correlations have a gradient of unity and demonstrate the additivity of $\bar{V}^\circ$ values of the pentaamminecobalt(III) complex. The intercept of eq 19 is significantly lower than that of eq 18. This reflects the strong electrostriction due to the 3+-charged complex. The magnitude of ΔV in Table V is slightly negative for the neutral leaving ligand RCOOH, whereas it is significantly negative for the uninegative leaving ligand $RCOO^-$. This tendency also demonstrates the role of electrostriction.[19] In the former, the charge on the complex is conserved during the reaction, whereas in the latter charge separation occurs and electrostriction is enhanced. The $\Delta V^\ddagger$ values in Table V are obtained at 65–80 °C, whereas the ΔV values are obtained at 25 °C. Recently, we have obtained the $\Delta V^\ddagger$ value of reaction 1 for X = Cl^-, Br^-, NO_3^- at relatively high temperatures (40–65 °C).[20] The results were similar to those already known at 25 °C, and the temperature effect on the $\Delta V^\ddagger$ values of these reactions is not significant. Therefore, neglecting the temperature effect on $\Delta V^\ddagger$, we can check the applicability of eq 2. As illustrated in Figure 2, the data points are fairly close to the line representing eq 2. Thus, eq 2 is also valid for these reactions treated in the present work. Alternatively, when the present results are combined with previous ones, a correlation can be obtained:

$$\Delta V^\ddagger = (0.48 \pm 0.02)\Delta V + (1.5 \pm 0.3) \quad (20)$$

Equation 20 is essentially analogous to eq 2. According to the consideration as given in the Introduction, eq 20 underlines the interchange character for the 24 aquations of $Co(NH_3)_5X^{n+}$.

Registry No. $Co(NH_3)_5(HCOO)^{2+}$, 19173-64-9; $Co(NH_3)_5(CH_3COO)^{2+}$, 16632-78-3; $Co(NH_3)_5(C_2H_5COO)^{2+}$, 19173-62-7; $Co(NH_3)_5(CH_2ClCOO)^{2+}$, 19173-67-2; $Co(NH_3)_5(CH_2BrCOO)^{2+}$, 19173-69-4; $Co(NH_3)_5(CHCl_2COO)^{2+}$, 19173-68-3; $Co(NH_3)_5(CHBr_2COO)^{2+}$, 19173-70-7; $Co(NH_3)_5(CCl_3COO)^{2+}$, 19998-53-9; $Co(NH_3)_5(CF_3COO)^{2+}$, 19173-66-1; $[Co(NH_3)_5H_2O](ClO_4)_3$, 13820-81-0; $CH_2ClCOONa$, 3926-62-3; $CHCl_2COONa$, 2156-56-1; CCl_3COONa, 650-51-1; CF_3COONa, 2923-18-4; $CHBr_2COONa$, 631-64-1; $CH_2BrCOONa$, 79-08-3.

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Electron-Transfer Reactions of Technetium and Rhenium Complexes. 2.[1] Relative Self-Exchange Rate of the M(I)/M(II) Couples $[M(DMPE)_3]^{+/2+}$, Where M = Tc or Re and DMPE = 1,2-Bis(dimethylphosphino)ethane

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The relative rates of self-exchange of the closely related d^6/d^5 couples $[Tc(DMPE)_3]^{+/2+}$ and $[Re(DMPE)_3]^{+/2+}$ have been determined by two independent applications of the Marcus theory. (1) The rates and equilibrium constants governing the cross-reactions between $[Re(DMPE)_3]^+$ and $[(NH_3)_5RuL]^{3+}$ (L = 4-picoline, pyridine, and isonicotinamide) were measured in a 0.100 M LiCl and 0.001 M HCl aqueous medium and compared to equivalent data previously obtained for the reaction of $[Tc(DMPE)_3]^+$ with the same three Ru(III) complexes in this medium. Independent electrochemical measurements show that in this medium the difference in reduction potential $E_{Tc}^{\circ\prime} - E_{Re}^{\circ\prime}$ is 80 ± 2 mV. Application of the Marcus cross relationship to these data leads to three independently determined values of k_{ex}^{Re}/k_{ex}^{Tc}: 2.1 ± 0.3, 1.3 ± 0.2, and 3.2 ± 0.8 for the 4-picoline, pyridine, and isonicotinamide complexes, respectively. The weighted average of these determinations, 1.6 ± 0.2, provides the best composite estimate of the kinetically determined k_{ex}^{Re}/k_{ex}^{Tc} ratio. (2) EXAFS measurements were used to obtain average Re(I)–P and Re(II)–P bond lengths for the $[Re(DMPE)_3]^{+/2+}$ complexes, and these data were compared to equivalent data available for the $[Tc(DMPE)_3]^{+/2+}$ complexes. The difference in bond lengths, $(M^{II}\text{–}P) - (M^{I}\text{–}P)$, is less for the Re couple than for the Tc couple (0.054 vs 0.068 Å), and within the Marcus formalism this leads directly to a structurally determined value of $k_{ex}^{Re}/k_{ex}^{Tc} = 2$. Thus, the kinetically observed, slightly greater rate of self-exchange of the $[Re(DMPE)_3]^{+/2+}$ couple is seen to be due entirely to the somewhat smaller structural distortions suffered by the inner coordination sphere of the Re complex during electron transfer. The absolute self-exchange rates of the $[Re(DMPE)_3]^{+/2+}$ and $[Tc(DMPE)_3]^{+/2+}$ couples are calculated to be 4×10^6 M^{-1} s^{-1} and 2×10^6 M^{-1} s^{-1}, respectively (25 °C, μ = 0.10 M).

Introduction

During the past 3 decades there has been considerable interest in determining the rates of self-exchange reactions for outer-sphere redox couples, and in providing a theoretical framework for understanding these fundamental electron transfer reactions.[5] Despite the extensive compilation of experimentally determined self-exchange rates that has resulted from this interest, there are no examples known to us that meet the following criteria: (i) identical experimental procedures and conditions are used to determine the relative $E^{\circ\prime}$ values and self-exchange rates of two analogous redox couples, the central metals of which are second-

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