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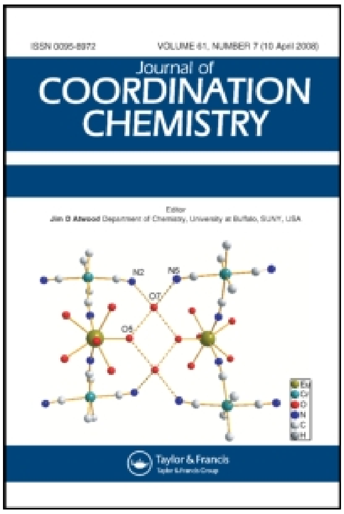

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KINETICS OF THE CHROMIUM(II) REDUCTIONS OF CHELATED AMINO ACIDO-BIS(ETHYLENE-DIAMINE)COBALT(III) COMPLEXES

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KINETICS OF THE CHROMIUM(II) REDUCTIONS OF CHELATED AMINO ACIDO-BIS(ETHYLENE-DIAMINE)COBALT(III) COMPLEXES

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The kinetics of Cr^{2+}(aq) reductions of glycinato-, D,L-alanato, D,L-phenylalanato-, and D,L-leucinatobis-(ethylenediamine)cobalt(III) ions have been investigated. The rate law is of the form $d(\ln[Co(III)]/dt = k[Cr^{2+}]$, where the rate constant $k(M^{-1} sec^{-1})$ and associated activation parameters $\Delta H^{\ddagger}$(kcal mol^{-1} and $\Delta S^{\ddagger}$-(cal deg^{-1}mol^{-1}) in parentheses, are respectively 1.65 ± 0.06 (9.7 ± 0.1, −25 ± 1), 0.367 ± 0.008 (10.9 ± 0.4, −24 ± 1), 0.529 ± 0.021 (11.2 ± 0.4, −22 ± 1); and 0.358 ± 0.019 (11.5 ± 0.3, −22 ± 1) at 298°K and $\Sigma [ClO_4^-] = 1.0$ M. The reactions are all inner-sphere.

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INTRODUCTION

During the past five years there has been an increasing interest in the chromium(II) reductions of cobalt(III) amino acid complexes, as well as in the chemistry of amino acid complexes of chromium(III). Gilroy, Sedor, and Bennett[1] first reported the chromium(II) reduction of glycinatobis(ethylenediamine)cobalt(III). Shortly thereafter Holwerda, Deutsch, and Taube[2] reported the analogous reductions of glycinato and N-methyl substituted glycinatopentaamine-cobalt(III) ions. Bembi and Malik[3] and Malik, Bembi, and Sushila[4] have more recently reported the chromium(II) reductions of a series of penta- and tetraammine-cobalt(III) amino acid complexes.

In a follow-up study of the chromium(III) products of the $Coen_2gly^{2+}$–Cr^{2+} reaction[1] Lane, Sedor, Gilroy, and Bennett[5] have characterized $Cr(H_2O)_5glyH^{3+}$ and have further noted that upon prolonged standing the monodentate species equilibrates with the chelated species $Cr(H_2O)_4gly^{2+}$. Additional recent interest in glycinatochromium(III) species is to be noted.[6–9] In the present work we report our kinetic results for the chromium(II) reductions of a short series of chelated amino acidobis(ethylenediamine)cobalt(III) complexes.

EXPERIMENTAL

Materials

The complexes $[Coen_2(A–A)]I_2$ (where A–A = the anion of glycine and D,L-leucine, D,L-alanine, D,L-phenylalanine, respectively) were prepared by the method of Liu and Douglas.[10] The perchlorate salt of the alanato complex was prepared by reacting a solution of the iodide salt with silver perchlorate in slight excess. The precipitated silver iodide was filtered off and the filtrate chilled to obtain crystals which were washed with absolute alcohol and anhydrous ether. The salt crystallizes as the dihydrate.[11] Solutions of the remaining complexes containing only the perchlorate anion were prepared by passing solutions containing 0.1 – 0.2 mmole of the respective iodide salt through a 1 x 5 cm anion exchange resin (Dowex 2–X8, 50–100 mesh, $C\ell O_4^-$ form) and rinsing the column with triply distilled water. The spectra obtained from solutions prepared in this manner exhibited molar absorptivities slightly lower than those reported by Liu and Douglas.[10] No traces of iodide ion were detected in these solutions when aliquots (0.02 mmole of complex ion) were treated with 0.1 M silver nitrate.

Solutions of sodium perchlorate, perchloric acid, and chromium(II) perchlorate were all prepared from reagent grade chemicals as described previously.[12] Tap distilled water was redistilled from alkaline permanganate and then from dilute sulfuric acid in an all pyrex apparatus.

Kinetics

Kinetics experiments were generally performed by pipetting aliquots of complex ion, perchloric acid,

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sodium perchlorate, and triply distilled water into a five centimeter spectrophotometric cell. The cell was then capped with a self sealing rubber septum and its contents purged with water-saturated, prepurified argon (delivered through a 3″ stainless steel needle) for 15–20 min. After the cell was brought to reaction temperature in the thermostatted cell compartment of a Cary 14 recording spectrophotometer, a thermostatted aliquot of chromium(II) perchlorate was injected into the cell by means of a simple transfer syringe technique. The cell was momentarily taken out of the compartment, inverted, shaken vigorously (to ensure thorough mixing), and then returned for continuous absorbance measurements at 487–488 nm. After ten half-lives or longer, the cell cap was removed and a thermometer (± 0.1°C and very near reaction temperature) was inserted into the neck of the cell and allowed to equilibrate for 5 min. whereupon the temperature was recorded. (The gap in the cell compartment was covered with a towel during the above procedure). All kinetics runs were performed with Cr^{2+} in excess so that pseudo first-order kinetics were obeyed. Plots of log $(A_t - A_\infty)$ *vs.* time, where A_t and A_∞ are the absorbances at times *t* and after ten half-lives, respectively, were linear for $> 3t_{1/2}$'s.

Stoichiometries

Special scans of the product solutions were obtained following certain kinetics runs in the wavelength range 475–350 nm. Since both Cr^{2+} and Co^{2+} have known, low molar absorptivities in this region, the observed absorbances were corrected for them. The resulting spectra were *assumed* to be those of $Cr(H_2O)_5A{-}AH^{3+}$ species.

RESULTS AND DISCUSSION

From Table I it can be seen that the visible absorption spectrum of the $Coen_2gly^{2+}{-}Cr^{2+}$ product solution is in close agreement with $\lambda_{max} = 572$ nm ($22.0\ M^{-1}cm^{-1}$) and $\lambda_{max} = 412$ nm ($23.0\ M^{-1}cm^{-1}$) reported by Lane, Sedor, Gilroy and Bennett[5] for $Cr(H_2O)_5glyH^{3+}$. Such agreement is consistent with the quantitative transfer of glycine from Co(III) to Cr(III) *via* an inner-sphere mechanism. The other spectra are *assumed* to be those of $Cr(H_2O)_5A{-}AH^{3+}$ species due to the close agreement between their λ_{max} and ϵ values and those of the glycine complex. Therefore the stoichiometries may be represented by Eq. 1.

$$Coen_2(A{-}A)^{2+} + Cr^{2+} + 3H^+ \rightarrow CrA{-}AH^{3+} + Co^{2+} + 2enH^+ \quad (1)$$

In Table II are summarized the individual kinetic runs for the titled reactions. The limited data for the glycinato reaction is included since the earlier reports[1a,b] were carried out in a Li^+/H^+ medium. A comparison of k_{obs} *vs.* $[Cr^{2+}]$ (Col. 5 and 3) clearly indicates the reactions to be first-order in $[Cr^{2+}]$, as does the constancy of *k* ($k_{obs}/[Cr^{2+}]_{eff}$) in column 6. Since the [Co(III)] was not negligible compared to $[Cr^{2+}]$, $[Cr^{2+}]_{eff}$ was taken to be $[Cr^{2+}]_0 - [Co(III)]_0/2$ in calculating the values of *k*. The values of k_{obs} are independent of $[H^+]$ in the range 0.070 – 0.700 M (Cf. columns 4 and 5, Table II). Although it was not convenient to vary [Co(III)] significantly, the excellent first-order plots obtained for the disappearance of Co(III)

TABLE I
Spectra of amino acid complexes of $Coen_2(A{-}A)^{2+}$ and $Cr(H_2O)_5A{-}AH^{3+}$

Complex	λ_{max},nm(ϵ,$M^{-1}cm^{-1}$)[a]	Lit.: $\lambda_{max}(\epsilon)$[b]	Prod: $\lambda_{max}(\epsilon)$[c]
$Coen_2gly^{2+}$	489(92.8)	487(98.5)	574(22.0)
	347(103)	346(109.4)	411(23.7)
$Coen_2$D,L-ala^{2+}	488(109)	487(110.2)	575(24.0)
	348(114)	347(118.0)	412(25.2)
$Coen_2$D,L-$palan^{2+}$	488(107)	488(104.4)	574(24.6)
	348(119)	347(118.0)	412(25.4)
$Coen_2$ D,L-$leuc^{2+}$	487(104)	487(108.8)	574(25.1)
	348(114)	346(129.2)	410(24.7)

[a] Perchlorate as only anion.
[b] Ref. 10, iodide salts.
[c] Products of the $Coen_2(A{-}A)^{2+}{-}Cr^{2+}$ reactions, $\Sigma[ClO_4^-] = 1.0$ M. Avg. of duplicate expts. with deviations for $\lambda \leqslant \pm 1.4$.

TABLE II

Kinetics experiments for the reaction between Coen$_2$(A–A)$^{2+}$ and Cr^{2+}. Where A–A = Glycinate, D,L-Alanate, D,L-Phenylalanate, and D,L-Leucinate at. Σ [ClO$_4^-$] = 1.0 M

A–A	t[a], °C	10[Cr^{2+}]$_0$, M	[H$^+$], M	$10^2 k^b_{obs}$, sec^{-1}	$10k^c$, M^{-1} sec^{-1}
Glycinate[d]	24.8	0.116	0.693	1.84	17.0
		0.116	0.693	1.78	16.5
		0.233	0.700	3.89	17.3
		0.116	0.250	1.76	16.3
		0.116	0.070	1.74	16.1
		0.116	0.693	1.75	15.8[e]
	15.1	0.116	0.693	1.03	9.47
		0.233	0.700	2.14	9.49
	34.5	0.233	0.700	6.56	29.0
		0.116	0.693	3.13	29.1
D,L-Alanate[d]	24.8	1.00	0.703	3.70	3.70
		1.00	0.703	3.75	3.75
		0.746	0.700	2.72	3.69
		0.456	0.700	1.71	3.81
		0.116	0.693	0.393	3.64
		0.233	0.250	0.808	3.59
		0.233	0.070	0.802	3.57
		0.233	0.700	0.831	3.64[e]
	15.0	0.456	0.700	0.811	1.81
		0.233	0.700	0.413	1.84
	35.0	0.233	0.700	1.58	6.99
		0.116	0.693	0.706	6.48
D,L-Phenylalanate[f]	24.8	0.746	0.700	4.08	5.00
		0.233	0.700	1.18	5.22
		0.116	0.693	0.551	5.52
		0.233	0.250	1.18	5.22
		0.233	0.070	1.17	5.20
		0.233	0.700	1.26	5.56[g]
	15.0	0.456	0.700	1.26	2.81
		0.233	0.700	0.615	2.72
	34.7	0.233	0.700	2.54	1.12
		0.116	0.693	1.04	0.959
D,L-Leucinate[h]	24.8	0.746	0.700	2.63	3.56
		0.456	0.700	1.54	3.43
		0.233	0.700	0.803	3.55
		0.116	0.693	0.400	3.67
		0.233	0.250	0.824	3.64
		0.233	0.070	0.819	3.62
		0.233	0.700	0.822	3.60[i]
	15.0	0.456	0.700	0.813	1.81
		0.233	0.700	0.413	1.83
	34.8	0.233	0.700	1.59	7.06
		0.116	0.693	0.766	7.03

[a] Temperature ± 0.1°C.

[b] From d(ℓn[Co(III)]) = k_{obs}dt.

[c] $k_{obs} = k[\mathrm{Cr}^{2+}]_{eff}$; see text.

[d-i] Co(III) concentrations:

[d] 1.50×10^{-3} M.

[e] 1.01×10^{-3} M.

[f] 1.33×10^{-3} M.

[g] 9.00×10^{-4} M.

[h] 1.45×10^{-3} M.

[i] 9.83×10^{-4} M.

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verify the assumed first-order dependence on [Co(III)]. Thus the rate law for these reactions is –d[Co(III)]·/dt = k[Co(III)] [Cr^{2+}].

The activation parameters were computed by a linear least squares program employing the logarithmic form of the Eyring equation[13] and assuming $\kappa = 1$. The associated standard errors[14] were also computed by the program using an equal weighting of the individual rate constants. The results are summarized in Table III along with comparisons with other related systems. Unfortunately, the data reported by Malik, Membi, and Sushila[4] for the $Co(NH_3)_4(A-A)^{2+}-Cr^{2+}$ reactions appear to be in error and are not included in Table III.[15]

A striking feature of the present work is the near constancy of the k values as the substituent on the alpha carbon of the chelated amino acid is varied from $-H$ to $-CH_3$ to $-CH_3C_6H_5$ to $-CH_2-CH_2-CH(CH_3)_2$. (Cf. entries 1b–4, Table III). Fortuitously, the constants for the last three systems are virtually identical to that for the $Co(NH_3)_5Ac^{2+}-Cr^{2+}$ reaction (entry 16). Steric accessibility of the carbonyl group in the chelated glycinato species probably accounts for its rate enhancement relative to the other species, although neither the steric nor the other classical substituent effects correlate the data. The proximity of the constants in this study to those of the related pentaammine systems is likely the result of two opposing factors.

The "locked-in" carboxylato ligands tend to enhance the rate of electron transfer, whereas the so-called "chelate effect" of ethylenediamine tends to hinder the rate of electron transfer through constraints on Co–N bond stretching trans to the bridging group.[19] The entropy differences between the chelated and monodentate amino acid complexes reflect a substantially lower ordering requirement for the former in the activation process. The lowered entropy requirement is more than sufficient to overcome a 3 kcal mol^{-1} increase in $\Delta H^{\ddagger}$, thus accounting for the faster electron transfer rates of the chelated species.

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TABLE III

A comparison of rate constants and activation parameters for the reactions of $Co(NH_3)_5(A-AH)^{3+}$ and $Coen_2(A-A)^{2+}$ with Chromium(II).[a]

Species		k,[b] $M^{-1}\,sec^{-1}$	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal deg^{-1} mol^{-1}	Ref.
1a.	$Coen_2gly^{2+}$	2.2 (Li^+)	8.8	–27	1
b.		1.65[c]	9.7	–25	f
2.	$Coen_2$ D,L-ala^{2+}	0.367[c]	10.9	–24	f
3.	$Coen_2$ D,L-$pala^{2+}$	0.529[c]	11.2	–22	f
4.	$Coen_2$ D,L-leu^{2+}	0.358[c]	11.5	–22	f
5.	$RoglyH^{3+}$	0.064[d](Li^+)	7.7	–38	2
6.	RoN-$MeglyH^{3+}$	0.044[d](Li^+)	8.0	–38	2
7.	RoN,N-Me_2glyH^{3+}	0.038[d](Li^+)	7.5	–40	2
8.	RoN,N,N-Me_3gly^{3+}	0.016[d](Li^+)	7.7	–41	2
9.	RoD,L-$alaH^{3+}$	0.049[e]	8.0	–37	3
10.	RoD,L-$leuH^{3+}$	0.055[e]	7.6	–37	3
11.	RoD,L-$ileuH^{3+}$	0.039[e]	8.6	–40	3
12.	RoD,L-$valH^{3+}$	0.042[e]	8.2	–38	3
13.	RoD,L-$SerH^{3+}$	0.060[e]	7.6	–37	3
14.	RoD,L-$threoH^{3+}$	0.033[e]	9.2	–43	3
15.	RoD,L-$argH^{3+}$	0.115[e]	6.7	–33	3
16.	$RoOAc^{2+}$	0.35[e]	8.2	–33	20

[a] At 25°C and $\mu = 1.0$ M (Na^+/H^+) except as noted; Ro = $Co(NH_3)_5{}^{3+}$.
[b] Defined by d(ℓn[Co(III)])/dt = k[Cr^{2+}].
[c] [H^+] = 0.07–0.700 M.
[d] [H^+] = 0.55 M.
[e] [H^+] = 0.1 M.
[f] This work.

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15. The values of $10^3 k$($M^{-1} s^{-1}$) ($\Delta H^{\ddagger}$, Kcal mol^{-1} and $\Delta S^{\ddagger}$, caldeg^{-1} mol^{-1}, respectively) for the $Co(NH_3)_4$-$(A-A)^{2+}$–Cr^{2+} reactions given in Ref. 4 at $\mu = 1.0$ M, $[H^+] = 0.1$ M, and 24°C are: 3.45 (3.0, −20.3); 2.00 (3.9, −24.2); 2.00 at 34°C (7.8, −37.1); 1.99 at 34°C (8.0, −37.8) for A–A = the anions of glycine, D,L-isoleucine, L-alanine, L-arginine, L-histidine, L-lysine, and L-valine, respectively. These constants are all at least a factor of one hundred lower than those reported in the present study and in Ref. 1, whereas the constants should be *greater* since tetraamminecobalt(III) complexes are generally more reactive than the corresponding bis(ethylenediamine)cobalt(III) complexes. If this is true, as seems likely, then the observed absorbance changes may correspond to spontaneous and/or chromium(II)-catalyzed aquations of the initial Cr(III)amino acid complexes. The acidity was only 0.1 M in their studies, and both the above processes should be dependent on a $[H^+]^{-1}$ term.[16–18] Moreover only Cr^{3+} was observed as a reaction product in their studies. It is noteworthy, however, that no follow-up reactions were observed in the present study, i.e. the A_{∞} values were constant after ten $t_{1/2}$'s even at the lowest acidities.
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An excellent paper, H. Ogino, K. Tsukahara, and N. Tanaka, *Bull. Chem. Soc. Jpn.*, **49**, 2743 (1976), was discovered after this paper was in proof.

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