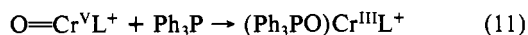
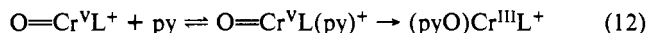


infrared and visible absorption spectra of the resulting light orange solution are the same as those obtained from the inner-sphere complex of (salen)Cr^{III} with triethylphosphine oxide. [The latter was synthesized directly from (salen)Cr(OH)₂⁺ and excess triethylphosphine oxide and showed a characteristic metal-coordinated (P=O)Cr stretching band at 1085 cm⁻¹ (note in free Et₃PO, ν_{P=O} = 1135 cm⁻¹) in the infrared spectrum and an absorption band at λ_{max} = 395 nm for (salen)Cr^{III} in the UV-visible spectrum.] We thus conclude that the coordination of phosphine is either accompanied by or rapidly followed by oxygen atom transfer so that the overall transformation is



A coordinated intermediate can be observed as a transient green

species when a large excess of pyridine is added to oxochromium(V), but it is rapidly converted to an orange complex, which we assign to the pyridine oxide adduct



Acknowledgment. We thank E. G. Samsel for the synthesis of the pyridine *N*-oxide adduct of Iif, J. D. Korp for the crystallographic structures in Figures 6 and 7, and the National Science Foundation and the R. A. Welch Foundation for financial support.

Supplementary Material Available: Tables of all bond distances, torsional and bond angles, anisotropic temperature factors, and observed and calculated structure factors (26 pages). Ordering information is given on any current masthead page.

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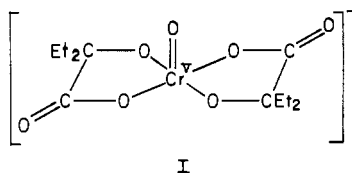
Electron Transfer. 75. Reduction of Carboxylato-Bound Chromium(V) with Vanadium(IV). Intervention of Chromium(IV)¹

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Received May 16, 1985

The chelated (carboxylato)chromium(V) anion bis(2-hydroxy-2-ethylbutyrate)oxochromate(V) (I), [(Lig)₂Cr(O)]⁻, reacts with oxovanadium(IV) to form a strongly absorbing species (λ_{max} = 515 nm; ε = 1.7 × 10³ M⁻¹ cm⁻¹) in the presence of 2-hydroxy-2-ethylbutyric acid buffers (pH 2-4). EPR data support 1:1 stoichiometry with VO²⁺ in deficiency, indicating the formation of a chromium(IV) species by a 1e reduction process. With excess VO²⁺ a chromium(III) product corresponding to a 2e reduction process was obtained. Spectral and ion-exchange properties of this product correspond to those observed for the titanium(III) and iron(II) reductions of chromium(V) and are consistent with the formulation of the product as a bis(hydroxycarboxylato) chelate of (H₂O)₂Cr^{III}. With excess vanadium(IV), the reaction exhibits triphasic kinetics. Two components of the triphasic profile are attributed to the parallel formation of chromium(IV) species from a slowly equilibrating ligation process: (Lig)₂Cr(O)⁻ + Lig⁻ ⇌ (Lig)₃Cr(O)²⁻. The equilibrium constant, 51 ± 7 M⁻¹ for this process, evaluated spectrophotometrically, was consistent with the values 46 and 64 M⁻¹ generated from the kinetic profile. The remaining step of the reaction is the reduction of the chromium(IV) intermediate with VO²⁺. Rates for all three steps increase with decreasing [H⁺] and level off at low [H⁺]. The limiting rate constants for the formation of the chromium(IV) intermediate by the (Lig)₃Cr(O)²⁻ and (Lig)₂Cr(O)⁻ pathways are 2.8 × 10³ and 2.2 × 10² M⁻¹ s⁻¹. The bimolecular limiting rate constant for the reduction of chromium(IV) is computed to be 7.7 × 10² M⁻¹ s⁻¹. Like the iron(II)-chromium(V) redox couple, the vanadium(IV) reduction of Cr(V) is taken to be an inner-sphere process.

The facile synthesis of water-soluble complexes of chromium(V), reported in 1979,² made available an additional unusual oxidation state to workers dealing in electron-transfer processes. Of particular interest are the reactions of Cr(V) with 1e reductants, for these must, in principle, proceed through the even rarer oxidation state chromium(IV). Although the reactivity of the latter has thus far precluded its detection in reactions of Cr(V) with Ce(III)³ and Ti(III),⁴ a transient species having properties corresponding to a complex of Cr(IV) was detected in reductions of Cr(V) chelate I with Fe(II).⁵ In the present study, which pertains to the reaction



of VO²⁺ with chelate I, we find evidence for intervention of the same, or a closely related, transient. The system at hand appears to be somewhat more complex than the earlier Cr(IV)-Fe(II) reaction, but it is more amenable to examination with ESR spectroscopy.

Experimental Section

Materials. Sodium bis(2-ethyl-2-hydroxybutyrate)oxochromate(V) (complex I) was prepared as its monohydrate as described;² good-quality

crystals of this complex were obtained by dissolving the complex in acetone at room temperature, gradually adding chloroform to incipient crystallization, and then slowly cooling to 0 °C. This chelate was kept in the dark at 0 °C. Aqueous solutions of the complex exhibited a maximum at 510 nm with an extinction coefficient of 161 M⁻¹ cm⁻¹ (lit.² 168 M⁻¹ cm⁻¹); this value rose to 189 M⁻¹ cm⁻¹ in the presence of a large excess of carboxylato ligand, reflecting a ligation equilibrium (see below).⁶ Solutions of VO(ClO₄)₂ were prepared by treating VOSO₄ (Alfa) with an equivalent quantity of Ba(ClO₄)₂ and then removing the precipitated BaSO₄.⁷ Concentrated vanadyl solutions could be analyzed spectrophotometrically for VO²⁺ in 1 M HClO₄ (ε₇₆₀ = 17.2 M⁻¹ cm⁻¹),⁸ whereas more dilute solutions were analyzed as the hydroperoxy complex as described.⁹ Solutions of Eu(ClO₄)₂ were prepared by the method of Fan.¹⁰ Lithium perchlorate, for use in kinetic experiments, was prepared by the method of Dockal¹¹ and recrystallized twice before use. Cation-

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- (6) Aqueous solutions of Cr(V) chelate I, if stabilized by 0.05 M 2-ethyl-2-hydroxybutyric acid at pH 3, decompose only slowly in the dark but undergo rapid decomposition to Cr(III) species in direct sunlight.
- (7) This precipitation is best carried out by adding a slight excess of Ba(ClO₄)₂ solution to aqueous VOSO₄, removing the precipitated BaSO₄ by centrifugation (rather than by filtration), adding additional VOSO₄ dropwise until no further precipitate forms, cooling to 0 °C, and then centrifuging once more.
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Table I. Stoichiometry of the Reaction of Chromium(V) Chelate I with Vanadium(IV)^a

$10^3[\text{Cr(IV)}]$, M	$10^3[\text{V(IV)}]$, M	$10^3[\text{V(IV)}]_{\text{rem}}$, M ^b	$\Delta[\text{V(IV)}]/$ $\Delta[\text{Cr(V)}]^c$
0.91	10.8	8.65	2.2
1.82	10.8	7.07	2.05
2.73	10.8	5.26	2.03
3.64	10.8	3.95	1.89
3.64	7.4	0.15	1.99

^aChromium(V) was added as sodium bis(2-ethyl-2-hydroxybutyrate)oxochromate(V) (I). Reactions were carried out in solutions 0.10 M each in the parent hydroxy acid and its salt at pH 3.4; $\mu = 1.0$ M (LiClO_4). ^bConcentration of V(IV) remaining; determined spectrophotometrically at 775 nm (see Experimental Section). ^c $\Delta[\text{V(IV)}] = [\text{V(IV)}]_{\text{taken}} - [\text{V(IV)}]_{\text{rem}}$.

exchange resin (Bio-Rad 50W-X2; 200–400 mesh), used in separation of reaction products, was pretreated as described.¹² The hydroxy carboxylic acid 2-hydroxy-2-ethylbutyric acid (Aldrich) was used as received, but concentrations were checked acidimetrically.

Physical Measurements. Spectral measurements were carried out with either a Cary 14 or Beckman UV 5260 spectrophotometer. A Durrum stopped-flow spectrophotometer was employed for kinetic measurements on rapidly reacting systems. X-Band ESR spectra were recorded on a Varian V-4500 spectrometer interfaced with a 489 Heath microcomputer. The g values of the signals were calibrated with deuterated 2,2,6,6-tetramethyl-4-oxo-1-piperidinyloxy ("Tempone") as an external standard¹³ having an isotropic g value of 2.0068.

Stoichiometric Studies. The stoichiometry of the reaction of chromium(V) chelate I with excess V(IV) was evaluated spectrophotometrically at pH 3.4 in the presence of an equimolar mixture (0.10 M) of 2-hydroxy-2-ethylbutyric acid and its sodium salt. The ionic strength was maintained at 1.0 M with LiClO_4 . Vanadium(IV) forms a complex with this hydroxy acid (see below), which exhibits an absorption maximum at 775 nm ($\epsilon = 22 \text{ M}^{-1} \text{ cm}^{-1}$). Absorbance decreases resulting from addition of known quantities of Cr(V) indicate that very nearly 2.0 mol of vanadium(IV) is consumed for each mole of Cr(V) taken (Table I).

ESR Studies. The Cr(V)–V(IV) reaction with V(IV) in deficiency was monitored by ESR spectroscopy to follow the disappearance of the Cr(V) signal, with single main peak $g = 1.98$ and line width 2.5 G, with four small lines due to the hyperfine coupling with ⁵³Cr ($I = 3/2$, 9.54% natural abundance; hyperfine coupling constant 14 Gauss), and the appearance of the eight-line¹⁴ VO^{2+} signal. Aqueous solutions of Cr(V) chelate I in a buffer containing the parent hydroxy acid and its sodium salt were mixed with known concentrations of VO^{2+} , the $[\text{VO}^{2+}]/[\text{Cr(V)}]$ ratio being varied from 0 to 3.0 but the total volume being kept constant. ESR spectra were taken immediately after mixing. Table II records the decrease in the relative intensity of the Cr(V) signal as VO^{2+} is added. No signals attributable to Cr(IV) or Cr(III) were observed, and the VO^{2+} signal did not appear unless the $[\text{VO}^{2+}]/[\text{Cr(V)}]$ ratio exceeded 2.0.

Examination of the Cr(III) Reaction Products. A reaction mixture that was 0.010 M in the Cr(V) complex (I), 0.020 M in $\text{VO}(\text{ClO}_4)_2$, 0.050 M in the ligand acid (2-ethyl-2-hydroxybutyric acid), and 0.050 M in its sodium salt had a pH of 3.4 and exhibited, 5 min after mixing, an absorption maximum at 585 nm ($\epsilon = 49 \text{ M}^{-1} \text{ cm}^{-1}$) and a minimum at 505 nm ($\epsilon = 27 \text{ M}^{-1} \text{ cm}^{-1}$).¹⁵ When this mixture was subjected to cation-exchange chromatography at 3 °C,¹⁶ a green eluate passed through the column quickly, the "leading" portion of this eluate being mixed with anionic or uncharged vanadium(V)-containing species. The chromium complex in this portion exhibited maxima at 588 nm ($\epsilon = 49 \text{ M}^{-1} \text{ cm}^{-1}$) and 415 nm ($\epsilon = 61 \text{ M}^{-1} \text{ cm}^{-1}$) very soon after elution and constituted between 50 and 60% of the Cr(V) taken. These peaks shifted,

Table II. Relative Intensities of Chromium(V) ESR Signals on Treatment with Vanadium(IV) (25 °C)^a

pH ^b	$10^3[\text{V(IV)}]$, M	$[\text{V(IV)}]/$ $[\text{Cr(V)}]$	rel peak height
3.4	0.0	0	100
	1.0	0.10	92
	2.0	0.20	82
	2.5	0.25	78
	3.0	0.30	74
	4.0	0.40	67
	5.0	0.50	58
	7.5	0.75	43
	10.0	1.00	26
	15.0	1.50	8
3.0	17.5	1.75	0
	0.0	0	100
	2.5	0.25	81
	5.0	0.50	67
	7.5	0.75	55
	10.0	1.00	41
	15.0	1.50	26
	17.5	1.75	4

^aSignal from sodium bis(2-ethyl-2-hydroxybutyrate)oxochromate(V) (complex I) was observed at $g = 1.98$, line width 11 G (see Experimental Section). $[\text{Cr(V)}]$ was 0.010 M throughout. ^bBuffer solutions were made from measured quantities of 2-ethyl-2-hydroxybutyric acid ($\text{pK}_A = 3.4$) and its sodium salt.

when the solution was allowed to stand 8 h at pH 2, to 570 nm ($\epsilon = 24 \text{ M}^{-1} \text{ cm}^{-1}$) and 412 nm ($\epsilon = 33 \text{ M}^{-1} \text{ cm}^{-1}$). A second band was rapidly eluted with 0.5 M HClO_4 and exhibited peaks at 581 nm ($\epsilon = 37 \text{ M}^{-1} \text{ cm}^{-1}$) and 414 nm ($\epsilon = 48 \text{ M}^{-1} \text{ cm}^{-1}$). Addition of 0.24 M HClO_4 to the reaction mixture before chromatography did not significantly affect the overall elution behavior. No appreciable CrO_4^{2-} was detected in reaction mixtures for which the $\text{VO}^{2+}/\text{Cr(V)}$ ratio exceeded 2.0.

The spectrum of the principal product, and its elution characteristics, were indistinguishable from those observed when the same Cr(V) complex was reduced, in the presence of excess ligand acid, with $\text{Eu}(\text{ClO}_4)_2$ (under N_2), with TiCl_3 ,⁴ or with $\text{Fe}(\text{ClO}_4)_2$.⁵ The Cr(V)– VO^{2+} product was, however, different (Table VI) from that formed from reduction by Eu^{2+} in the absence of excess ligand acid and from the monodentate 2-ethyl-2-hydroxybutyrate complex of $(\text{H}_2\text{O})_2\text{Cr}^{\text{III}}$, prepared from the parent carboxylic acid and $\text{Cr}(\text{ClO}_4)_3$ by the procedure of Hamm and co-workers.¹⁷

Kinetic Measurements and Estimation of Specific Rates. Reactions were monitored by following absorbance changes at 490 nm. Total ionic strength was maintained at 1.0 M by addition of LiClO_4 . When VO^{2+} was taken in excess, a rapid increase in absorbance, followed by a steep decrease (a pattern similar to that in the $\text{Fe}^{\text{II}}\text{–Cr}^{\text{V}}$ reaction)⁵ was observed, pointing to the growth and decay of a strongly absorbing intermediate. However, these steps were followed by a much slower decrease involving an absorbance change less than 10% of those associated with the principal components; the magnitude of this slow change did not depend upon the concentration of VO^{2+} taken. Depending on reagent concentrations, maximal absorbances occurred 0.2–0.8 s after mixing. With VO^{2+} in large excess, kinetic profiles were treated as composites of three consecutive steps, each of them a first-order or pseudo-first-order process. Rate constants under these conditions were evaluated with use of an iterative nonlinear least-squares fit¹⁸ of eq 1, where D and D_∞ are

- (17) Hamm, R. E.; Johnson, R. L.; Perkins, R. H.; Davis, R. E. *J. Am. Chem. Soc.* **1958**, *80*, 4469. In this instance, a 50-mL reaction mixture containing 2.5 mmol of $\text{Cr}(\text{ClO}_4)_3$ and 5.0 mmol of 2-ethyl-2-hydroxybutyric acid was maintained at 40 °C for 14 days, after which the desired carboxylato complex was separated from unreacted $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ by cation-exchange chromatography.
- (18) A nonlinear least-squares program (written in BASIC for the Apple II computer) was kindly provided by Professor J. H. Espenson and was used with minor modification. Trial values for k_3 were obtained from the slopes of logarithmic plots of absorbance difference vs. reaction times late in the reaction sequence when the first two kinetic components were very nearly negligible. Extrapolation of the same plots to $t = 0$ yielded a provisional value of D_∞ for the combination of the two initial steps. Estimates of k_1 and k_2 were then obtained from a nonlinear least-squares fit of expression 2. Values of k_1 and k_2 obtained from the final fit (eq

$$D = ae^{-k_1t} + be^{-k_2t} + D_\infty \quad (2)$$

1) were generally quite different (as much as 50% change) from the initial estimates. Agreement between initial estimates and the final fit for k_3 was within 10%. Individual data points were unweighted.

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- (15) A second maximum near 410 nm, ordinarily observed for Cr(III) complexes, was obscured in the "tail" of the strong vanadium(V) peak in the near-UV region.
- (16) Separations were carried out with use of Bio-Rad 50W-X2 sulfonate resin, H^+ form, 200–400 mesh, column length 5 cm, column capacity 2.0 mequiv. Use of a larger column led to more serious decomposition of the eluted Cr(III) complexes. For estimation of the extinction coefficients of Cr(III) species, aliquots of each eluted fraction were oxidized with basic H_2O_2 , and the total chromium content was determined as chromate. See, for example: Haupt, G. W. *J. Res. Natl. Bur. Stand., Sect. A* **1952**, *48*, 414.

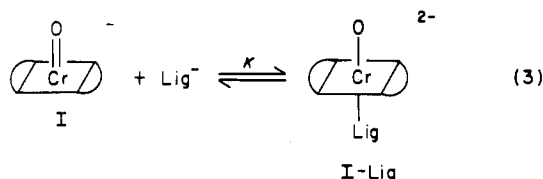
the absorbances at time t and at infinite time.

$$D = ae^{-k_1t} + be^{-k_2t} + ce^{-k_3t} + D_\infty \quad (1)$$

When the reaction was carried out with Cr(V) in large excess, an exponential growth of the intermediate was observed. Rate constants in such cases were obtained from slopes of semilogarithmic plots of absorbance differences vs. reaction times. Such plots were linear for more than 4 half-life periods. Unimolecular rate constants obtained from replicate runs agreed to better than 4%, but bimolecular specific rates for growth of the intermediate, calculated by dividing unimolecular values by the apparent value of $[\text{Cr}^{\text{V}}]$, were consistently 5–20% lower than those obtained from experiments with VO^{2+} in excess.¹⁹

The reaction between Eu^{2+} and Cr(V) complex I was too rapid to monitor with our equipment. When equal volumes of 10^{-4} M $\text{Eu}(\text{ClO}_4)_2$ and 10^{-4} M Cr(V) (each in a 0.01 M solution of the parent carboxylic acid) were mixed, reaction was more than 90% complete within 2 ms, implying a bimolecular rate constant greater than $5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ (22 °C). There was no indication of the formation of an intermediate in this reaction.

Spectral Changes of Cr(V) in the Presence of Excess 2-Hydroxy-2-ethylbutyrate. The apparent extinction coefficient associated with the 510-nm band of Cr(V) chelate I in water increases from 161 to 189 $\text{M}^{-1} \text{ cm}^{-1}$ upon addition of excess carboxylato ligand. Spectral data for this system, summarized in Table III, are in accord with partition of Cr(V) between two different ligation levels (equilibrium 3), which leads to eq 4. Here, A indicates the observed absorbance, $[\text{Cr}^{\text{V}}]_t$ the total Cr(V)



$$A = \epsilon_1 [\text{Cr}^{\text{V}}]_t + \frac{[\text{Cr}^{\text{V}}]_t [\text{Lig}^-] K}{1 + K [\text{Lig}^-]} (\epsilon_2 - \epsilon_1) \quad (4)$$

concentration, and ϵ_1 and ϵ_2 the extinction coefficients for chelate I and the "extraligated" species I-Lig²⁻, respectively. A nonlinear least-squares fit of eq 4 yielded $\epsilon_1 = 161 \pm 2 \text{ M}^{-1} \text{ cm}^{-1}$, $\epsilon_2 = 189 \pm 2$, and $K = 51 \pm 7 \text{ M}^{-1}$. Table III also compares observed absorbances with those calculated by using (4). Visible spectra of the chromium(V) chelate I were also measured in 0.1 M 2-hydroxy-2-ethylbutyrate in the presence of various known concentrations of the parent carboxylic acid, with the pH lying between 2.6 and 4.3. No significant spectral change was noted in this pH range.

Changes in the Spectrum of VO^{2+} with Addition of 2-Hydroxy-2-ethylbutyrate. The visible spectrum of VO^{2+} in ClO_4^- media features a band at 760 nm ($\epsilon = 17 \text{ M}^{-1} \text{ cm}^{-1}$) and a shoulder at 615 nm ($\epsilon = 9$). In 2-hydroxy-2-ethylbutyrate buffers, (pH 3.4), the band at 760 shifts to 775 nm, whereas the shoulder at 615 nm appears as a band at 620 nm; in addition, new bands at 520 and 400 nm develop. All four bands become more intense with increasing carboxylate concentration. If formation of a 1:1 complex is assumed, data at four wavelengths allow estimates of the formation constant of such a complex and its molar absorptivity. These are summarized in Table IV.²⁰

Estimation of $\text{p}K_A$ of the Intermediate. The visible spectrum of the strongly absorbing brown species formed by treatment of the Cr(V) chelate I with an equimolar quantity (or less) of VO^{2+} is perceptibly H^+ -dependent between pH 2 and 5. Since this intermediate decomposes

Table III. Absorbance Data for Mixtures of Chromium(V) Chelate I and 2-Hydroxy-2-ethylbutyrate^a

$10^3 [\text{Cr}^{\text{V}}]$, M	$[\text{Lig}^-]$, M	A_{obsd}	A_{calcd}^b
6.61	0 ^c	1.07	1.07
5.47	0.0050	0.90	0.93
5.58	0.0100	0.97	0.95
6.45	0.020	1.14	1.13
6.75	0.035	1.21	1.21
6.51	0.075	1.19	1.19
6.72	0.075	1.22	1.23
6.67	0.10	1.23	1.23
6.61	0.20	1.23	1.23
7.26	0.30	1.37	1.36

^aData were taken in a 100-cm cell at 21 °C. Equimolar concentrations of 2-hydroxy-2-ethylbutyrate (Lig^-) and its parent acid were maintained in each case. Absorbances were observed at 510 nm. ^bValues were calculated by using eq 4 in the text, taking ϵ_1 as $161 \text{ M}^{-1} \text{ cm}^{-1}$, ϵ_2 as $189 \text{ M}^{-1} \text{ cm}^{-1}$, and K as 51 M^{-1} . ^cNo buffer added; pH was adjusted to 3.0 with use of dilute HClO_4 .

Table IV. The 2-Hydroxy-2-ethylbutyrate Complex of VO^{2+}

λ , nm	ϵ , $\text{M}^{-1} \text{ cm}^{-1}$	K , M^{-1} ^a	λ , nm	ϵ , $\text{M}^{-1} \text{ cm}^{-1}$	K , M^{-1} ^a
775	22	46	575	15	45
625	19	45	520	21	32

^aEstimated association constant at 21 °C, pH 3.4, and $\mu = 1.0 \text{ M}$ (ClO_4^-).

Table V. Variation, with Acidity, of the Cr(IV) Spectrum (23 °C)^a

$10^4 [\text{H}^+]$, M	R_{obsd}^b	R_{calcd}^c	$10^4 [\text{H}^+]$, M	R_{obsd}^b	R_{calcd}^c
123	0.94	0.94	3.2	0.81	0.80
100	0.97	0.94	2.0	0.80	0.77
60	0.93	0.93	1.12	0.74	0.73
28	0.86	0.91	0.70	0.81	0.71
12.6	0.84	0.86	0.34	0.68	0.69

^aSolutions were 0.0074 M each in Cr(V) chelate (I) and $\text{VO}(\text{ClO}_4)_2$ and 0.40 M in 2-hydroxy-2-ethylbutyric acid. $[\text{H}^+]$ was adjusted by partial neutralization of the latter acid. ^bObserved ratio of absorbances at 500 and 440 nm. ^cAbsorbance ratio (500/440 nm), calculated by using eq 5, with R_B taken as 0.69, R_{BH} as 0.95, and K_A as $3.8 \times 10^{-4} \text{ M}$.

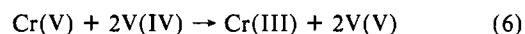
appreciably on the time scale needed for spectral measurements, its $\text{p}K_A$ value was estimated with use of the ratio of absorbances at 500 and 440 nm (this ratio, R , remains very nearly constant despite the perceived decay). The relationship employed is (5), in which R_B and R_{BH} represent

$$R = \frac{R_B K_A + R_{\text{BH}} [\text{H}^+]}{K_A + [\text{H}^+]} \quad (5)$$

this absorbance ratio for the basic and acidic forms of the intermediate. Absorbance data (Table V) lead to a K_A value of $(3.8 \pm 1.2) \times 10^{-4} \text{ M}$ ($\text{p}K_A$ 3.4, 23 °C, $\mu = 0.4 \text{ M}$) for this intermediate.

Results and Discussion

Stoichiometry experiments carried out with VO^{2+} in excess (Table I) indicate that 2 mol of V(IV) are consumed for each mole of Cr(V) taken. The principal net reaction, under these conditions, may be represented simply as (6). Since, however, V(IV) is



necessarily a one-electron reductant, a Cr(IV) intermediate must intervene (as is the case with reduction by Fe^{II}),⁵ and such intervention in the present system may be demonstrated not only by the observed kinetic profiles but also by the results of ESR studies.

The addition of 0.1–0.3 equiv of VO^{2+} to 1 equiv of Cr(V) is seen (Table II) to reduce the intensity of the Cr(V) ESR signal to a value indicating the consumption of nearly 1 Cr(V) per added VO^{2+} , i.e., under these conditions we are dealing with 1:1 stoichiometry:



(19) This discrepancy, which persisted despite several modifications in experimental technique, was most troublesome at high concentrations of added carboxylate ligand. It suggests the irreversible conversion of the principal rapidly reacting Cr(V) oxidant, in minor part, to a slowly reacting or nonreacting species, an effect observed during an earlier investigation.³ Since such a conversion should not affect specific rates for growth of the intermediate with V(IV) in excess, we have considered the latter as reliable, whereas those measured with Cr(V) in excess are suspect. Note also that growth of the intermediate with excess Cr(V) was followed by a slow decrease in absorbance, possibly reflecting disproportionation. The latter did not seriously complicate interpretation of kinetic results.

(20) The spectrum of the 2-hydroxy-2-ethylbutyrate complex of VO^{2+} was also found to be pH-dependent between pH 2.6 and 4.4. When the pH is increased from 2.6 and 3.8, the 775-nm band grows, whereas the remaining three visible bands shrink. Above pH 3.8, the 520- and 400-nm bands shrink and move gradually to greater wavelengths. However, we were unable to obtain limiting spectra in these cases and did not attempt to estimate the acidity constant(s) of the complex(es).

Table VI. Spectral Characteristics of Cr(III) Complexes

complex	generating reacn	ϵ_1	λ_1	ϵ_2	λ_2
Cr(H ₂ O) ₆ ³⁺		13.4	574	15.6	408
Cr(H ₂ O) ₅ (Lig) ²⁺ ^a		27	565	33	415
<i>cis</i> -Cr(H ₂ O) ₄ (HCO ₂) ₂ ^{+b}		27	574	27	413
Cr(H ₂ O) ₅ (gly) ²⁺ ^c		24.5	569	30.9	411
Cr(H ₂ O) ₄ (gly) ²⁺ ^c chelate		30.3	569	39.3	411
	Cr(V) + Eu ²⁺ (no added ligand) ^d	35	563	41	428
	Cr(V) + Eu ²⁺ (excess ligand) ^{d,e}	49	583	61	417
	Cr(V) + Ti(III) (excess ligand) ^{d,f}	48	583	62	413
	Cr(V) + Fe(II) (excess ligand) ^{d,e,g}	48	585	61	415
	Cr(V) + VO ²⁺ (excess ligand) ^{d,e,h}	49	588	61	415
Cr(ox) ₃ ³⁻ (trichelate) ⁱ		87	570	110	418

^aLig = 2-hydroxy-2-ethylbutyrate. Complex was prepared by the method of Hamm.¹⁷ ^bWard, J. R.; Haim, A. *J. Am. Chem. Soc.* **1970**, *92*, 475. ^cButler, R. D.; Taube, H. *J. Am. Chem. Soc.* **1965**, *87*, 5597. gly = glycolato. ^dReduction of Cr(V) chelate I. ^eReaction was carried out in 10-fold excess of ligand. ^fReference 4. ^gReference 5. ^hPresent work. ⁱSchlafer, H. L. *Z. Phys. Chem. (Wiesbaden)* **1957**, *11*, 65. ox = oxalato.

Table VII. Kinetic Data for Reduction of (Carboxylato)chromium(V) with VO²⁺ (21 °C, $\mu = 1.0$)

10 ³ [Cr ^V], M ^a	10 ³ [V ^{IV}], M	[Lig ⁻] ^b	[HLig] ^c	pH	10 ⁻³ k ₁ ' M ⁻¹ s ^{-1d}	10 ⁻³ k ₂ ' M ⁻¹ s ^{-1e}	k ₃ ' M ⁻¹ s ^{-1f}
0.25	2.18	0.050	0.050	3.40	1.24 (1.20)	0.44 (0.37)	51 (44)
0.25	4.36	0.050	0.050	3.40	1.24 (1.20)	0.40 (0.37)	53 (44)
0.25	8.12	0.050	0.050	3.40	1.12 (1.20)	0.50 (0.37)	44 (44)
0.46	4.35	0.050	0.20	2.80	0.58 (0.54)	0.12 (0.14)	13.3 (16.2)
0.46	4.35	0.050	0.150	2.92	0.63 (0.65)	0.16 (0.18)	19.8 (20.3)
0.39	4.35	0.050	0.100	3.10	0.87 (0.85)	0.23 (0.24)	23 (27)
0.43	4.35	0.050	0.050	3.40	1.18 (1.19)	0.37 (0.37)	44 (44)
0.43	4.35	0.050	0.025	3.70	1.52 (1.50)	0.47 (0.50)	58 (61)
0.43	4.36	0.015	0.015	3.40	0.79 (0.86)	0.28 (0.37)	76 (78)
0.45	4.36	0.025	0.025	3.40	0.93 (0.94)	0.31 (0.37)	67 (64)
0.39	4.36	0.035	0.035	3.40	1.19 (1.08)	0.35 (0.37)	53 (55)
0.44	4.36	0.075	0.075	3.40	1.28 (1.31)	0.33 (0.37)	32 (33)
0.44	4.36	0.100	0.100	3.40	1.36 (1.38)	0.38 (0.37)	18 (27)

^aChromium(V) was added as sodium bis(2-ethyl-2-hydroxybutyrate)oxochromate(V) (I). ^b2-Ethyl-2-hydroxybutyrate. ^c2-Ethyl-2-hydroxybutyric acid. ^dSecond-order specific rates for formation of the principal intermediate, estimated from analyses of the triphasic kinetic curves as $k_1/[VO^{2+}]$ (eq 1). Values in parentheses are calculated from rate law 8, with a taken as $98 \text{ M}^{-1} \text{ s}^{-1}$, b as 64 M^{-1} , c as $5.4 \times 10^{-4} \text{ M}$, and d as $6.8 \times 10^{-4} \text{ M}$ (see text). ^eSecond-order specific rates for consumption of the principal intermediate, estimated from analyses of the triphasic kinetic curves as $k_2/[VO^{2+}]$ (eq 1). Values in parentheses are calculated from rate law 11, with e taken as 0.27 s^{-1} and f as $3.5 \times 10^{-4} \text{ M}$. ^fSecond-order specific rates for the slow kinetic component in the triphasic kinetic curve, estimated as $k_3/[VO^{2+}]$ (eq 1). Values in parentheses are calculated from rate law 13, with g taken as 0.10 s^{-1} , h as 46 M^{-1} , j as $2.3 \times 10^{-4} \text{ M}$, and m as $4.6 \times 10^{-4} \text{ M}$ (see text).

However, at higher ratios of V(IV) to Cr(V), departures from this 1:1 stoichiometry become increasingly pronounced, doubtless reflecting the competing rapid reaction of Cr(IV) with V(IV). Moreover, when 2 equiv of V(IV) have been added, the eight-line VO²⁺ signal¹⁴ appears, confirming the 2:1 stoichiometry that obtains with excess V(IV).^{21,22}

As with the reactions of Cr(V) chelate I with Ti(III)⁴ and Fe(II),⁵ the relatively high extinction coefficients ($\epsilon_{588} = 49 \text{ M}^{-1} \text{ cm}^{-1}$; $\epsilon_{415} = 61 \text{ M}^{-1} \text{ cm}^{-1}$) of the Cr(III) product and the ease with which it is eluted from our sulfonate cation-exchange column indicate the principal reduction product to be a +1 dichelated complex of (H₂O)₂Cr^{III}. Table VI compares the spectral properties of a number of known (carboxylato)chromium(III) complexes with those of the Cr(III) product from reductions of Cr(V) chelate I. Nonchelated carboxyl complexes of (H₂O)₅Cr^{III} and bis(carboxylato) complexes of (H₂O)₄Cr^{III} exhibit ϵ values of 20–30, whereas chelated mono(carboxylato) complexes of (H₂O)₄Cr^{III} are characterized by molar absorptivities between 30 and 40 M⁻¹ cm⁻¹. Products from reductions of Cr(V) with VO²⁺ or Eu²⁺ in excess ligand are seen to absorb more intensely than either of these types but considerably less strongly than tris(carboxylato) trichelates. Slow decomposition of our products in aqueous solution and faster decay in contact with polysulfonic acid resin call

to mind similar behavior observed for previously described (carboxylato)chromium(III) complexes.²³

As was observed in the Fe(II)–Cr(V) system,⁵ a strongly absorbing species ($\lambda_{\text{max}} 515 \text{ nm}$, $\epsilon = (1.6 \pm 0.2) \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$)²⁴ is generated when chelate I is mixed with VO²⁺ in the presence of excess ligand. With Cr(V) in excess, exponential curves associated with the growth of this intermediate are obtained, whereas with VO²⁺ in excess, both the growth of this intermediate and its reduction by VO²⁺ may be monitored, after which a third (minor) kinetic component is perceived. The mode of formation of this intermediate, the ease with which it reacts with 1e reductants in excess, and the results of our ESR studies carried out with Cr(V) in excess leave little doubt that we are dealing with a Cr(IV) species in the present work as well as in the earlier Fe(II)–Cr(V) reactions.

Analysis¹⁸ of each of the kinetic profiles obtained with excess VO²⁺ yields three pseudo-first-order rate constants, two of which (k_1 and k_2) are 10–40 times as great as the third (k_3). All three are proportional to [VO²⁺]. Second-order specific rates, obtained

(21) No ESR absorbance attributable to Cr(IV) is observed in our systems at, or slightly below, room temperature, in accord with the presence of an even number of d electrons in this species.^{22a} Signals due to Cr(III) complexes in aqueous systems are generally exceptionally broad^{22b} and should not interfere with our monitoring of Cr(V).

(22) See, for example: (a) Drago, R. S. "Physical Methods in Chemistry"; W. B. Saunders: Philadelphia, 1977; Chapter 13. (b) Wu, M.-Y.; Paton, S. J.; Fanchiang, Y.-T.; Gelerinter, E.; Gould, E. S. *Inorg. Chem.* **1978**, *17*, 326.

(23) (a) See, for example: Holloway, W. F.; Srinivasan, V. S.; Gould, E. S. *Inorg. Chem.* **1984**, *23*, 2181. Gould, E. S. *J. Am. Chem. Soc.* **1968**, *90*, 1740 (footnote 10). (b) The discrepancy between λ_1 values (Table VI) for the Cr(III) product obtained from reduction by VO²⁺ (588 nm), as compared to those for the Fe(II)- and Ti(III)-generated products (583 nm), lies outside of experimental error. We suspect that the last two products may have undergone slight aquation before measurement, whereas the product from VO²⁺ (which was examined after we had gained more experience with such systems) has only a single component.

(24) The corresponding intermediate in the Fe(II)–Cr(V) system⁵ exhibits a maximum at 515 nm, $\epsilon = 1.5 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$. This intermediate persists only in the presence of excess Cr(V), which also absorbs strongly in the ultraviolet region. Because of this limitation, reliable UV spectra of the intermediate could not be obtained.

by dividing these values by $[\text{VO}^{2+}]$, are found to depend upon the concentrations of added carboxylate ligand and on $[\text{H}^+]$ for k_1 and k_3 (see below) but only upon $[\text{H}^+]$ for k_2 . Kinetic data are summarized in Table VII.

Runs carried out with Cr(V) in excess feature the exponential growth of the intermediate and allow us to assign k_1 to this process and k_2 to consumption of the intermediate by excess reductant.^{25,26} The nature of the (minor) k_3 component is, however, ambiguous. It could result from slow decay of a second intermediate which is formed rapidly or from rapid decay of an intermediate which is formed slowly.²⁶

The major component associated with growth of the Cr(IV) intermediate (the bimolecular rate constant for which may be designated k_1') conforms to eq 8, which may be rewritten in the algebraically equivalent form, eq 9, pertaining to the system at

$$k_1' = \frac{a[\text{Lig}^-]}{b[\text{Lig}^-](c + [\text{H}^+]) + d + [\text{H}^+]} \quad (8)$$

$$\text{rate} = \frac{[\text{Cr}]_T[\text{V}]_T k_{\text{lim}} K_L K_A [\text{Lig}^-]}{K_L [\text{Lig}^-] (K_A + [\text{H}^+]) + K_A' + [\text{H}^+]} \quad (9)$$

hand, where $[\text{Cr}^V]_T$ and $[\text{V}]_T$ are the total concentrations of added Cr^V and V^{IV} and $[\text{Lig}^-]$ is the concentration of added carboxylate anion. Nonlinear least-squares refinement^{27,28} of k_1' values yields $a = 98 \pm 9 \text{ M}^{-1} \text{ s}^{-1}$, $b = K_L = 64 \pm 14 \text{ M}^{-1}$, $c = K_A = (5.4 \pm 1.0) \times 10^{-4} \text{ M}$, and $d = K_A' = (6.8 \pm 1.8) \times 10^{-4} \text{ M}$. Table VII also compares observed rates with those calculated from (8). This rate law for growth of the intermediate is consistent with an activated complex formed from one unit each of Cr^V and V^{IV} with an additional unit of ligand and loss of one H⁺. Both the ligation (association constant K_L) and the deprotonation (acidity constant K_A) exhibit kinetic saturation in the concentration range studied. The second acidity constant, K_A' , pertains to deprotonation of the inactive species which has not acquired the extra unit of ligand.

Spectrophotometric data (Tables III and IV) indicate that both the Cr(V) chelate I and VO^{2+} undergo partial additional ligation²⁹ by added 2-hydroxy-2-ethylbutyrate at the concentrations of that anion taken during our kinetic runs. Association constants determined independently for these ligations (51 and 45 M^{-1}) lie close enough to our calculated value of K_L (64 M^{-1}) so that a direct choice between the two cannot be made. Although several formulations^{30,31} are possible, we suggest that the active oxidizing

agent in the principal conversion of Cr(V) to Cr(IV) is the "extraligated form", $(\text{Lig})_3\text{Cr}^V\text{O}$, of dichelate I ("I-Lig" in eq 3) from which one proton has been removed. If we assume that the K_L terms in (9) reflect ligation of the oxidant, we must conclude that the ligated and nonligated forms of V(IV) (Table IV) undergo oxidation at very similar specific rates, for if this were not so, a second ligation constant would appear in (8). The limiting specific rate, k_{lim} , for this reduction (at high $[\text{Lig}^-]$ and low $[\text{H}^+]$), calculated as $a/K_L K_A$, is $2.8 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ (21°C , $\mu = 1.0$).

The principal kinetic component reflecting the reduction of Cr(IV) to Cr(III) (bimolecular rate constant k_2') appears to follow the rate law (11) and its equivalent form (12), which suggests a transition state consisting of one unit each of Cr^{IV} and V^{IV}, formed with loss of a proton (characterized by acidity constant K_A). Refinement²⁷ of k_2' values yields $e = k_{\text{lim}} K_A = 0.27 \pm 0.04$

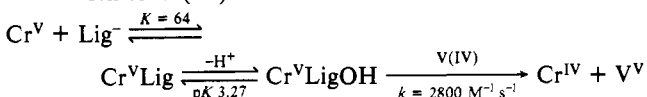
$$k_2' = \frac{e}{f + [\text{H}^+]} \quad (11)$$

$$\text{rate} = \frac{[\text{Cr}^{\text{IV}}]_T [\text{V}]_T k_{\text{lim}} K_A}{[\text{H}^+] + K_A} \quad (12)$$

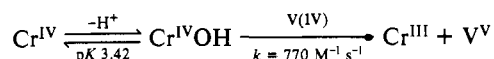
s^{-1} and $f = K_A = (3.5 \pm 1.4) \times 10^{-4} \text{ M}$. The latter agrees closely with the pK_A of the Cr(IV) intermediate determined spectrophotometrically ($3.8 \times 10^{-4} \text{ M}$, Table V). Although VO^{2+} has been shown to be partially converted to a carboxylate complex in the reaction medium, k_2' is found not to vary significantly with $[\text{Lig}^-]$, implying again that the unligated and ligated forms of V(IV) reduce Cr(IV) at closely similar rates.

Our data then allow us to represent the principal sequence in the overall conversion of Cr(IV) to Cr(III) schematically as follows (only the kinetically active ligand, Lig^- , is included):

Conversion to Cr(IV)



Reduction of Cr(IV)



Turning now to the slow (k_3') component, we note that it cannot be due to interconversion between Cr(III) products, for it is found to be first order in V(IV). Moreover, it cannot reflect conversion of one Cr(IV) intermediate to another in competition with reduction by V(IV), for if this were the case, it should become relatively less important at high concentrations of VO^{2+} , a trend that is not observed. We suspect instead that it represents reduction of the more sluggish Cr(V) species, i.e. dichelate I ($(\text{Lig})_2\text{Cr}^V\text{O}$). Appearance of this as a separate kinetic component requires that the equilibrium between species (eq 3) be established slowly in comparison to their reductions, a conclusion in accord with a recent study³² in which alteration of the ligand environment about chelated chromium(V) plays a part. This slow component proceeds as described by the rate law shown in eq 13 and 14, which

$$k_3' = \frac{g}{h[\text{Lig}^-](j + [\text{H}^+]) + m + [\text{H}^+]} \quad (13)$$

$$\text{rate} = \frac{[\text{Cr}^V]_T [\text{V}]_T k_{\text{lim}} K_A'}{K_L [\text{Lig}^-] (K_A + [\text{H}^+]) + K_A' + [\text{H}^+]} \quad (14)$$

corresponds to a transition state having the chromium(V) chelate (without the extra ligand) and a unit of V^{IV}, formed again with loss of a proton (acidity constant K_A'). Refinement²⁷ in this instance yields $g = k_{\text{lim}} K_A' = 0.10 \pm 0.02 \text{ s}^{-1}$, $h = K_L = 46 \pm 16 \text{ M}^{-1}$, $j = K_A = (2.3 \pm 1.2) \times 10^{-4} \text{ M}$, and $m = K_A' = (4.6 \pm 2.2) \times 10^{-4} \text{ M}$. Agreement between values of K_L , K_A , and K_A' obtained

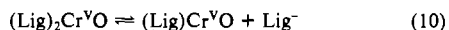
(25) The usual ambiguity associated with the assignment of rate constants to the components of a biphasic kinetic curve²⁶ becomes a sixfold ambiguity when we are dealing with the triphasic curves obtained with VO^{2+} in excess. This ambiguity is partially resolved by comparison of specific rates with those obtained with Cr(V) in excess, but a twofold ambiguity associated with the minor component remains.

(26) See, for example: Espenson, J. H. "Chemical Kinetics and Reaction Mechanisms"; McGraw-Hill: New York, 1981; pp 65-70.

(27) In these refinements, which minimized the function $[(k)_{\text{obsd}} - (k)_{\text{calcd}}]^2$, individual data points were unweighted. Values of $[\text{H}^+]$ were calculated from the concentrations of ligand carboxylic acid and its anion, taking K_A for the acid²⁸ as $5.0 \times 10^{-4} \text{ M}$.

(28) Srinivasan, V. S.; Gould, E. S. *Inorg. Chem.* **1981**, *20*, 3176.

(29) Our absorbance data for mixtures of chromium(V) chelate I and 2-hydroxy-2-ethylbutyrate (Table III) are consistent also with an equilibrium of type 10 with an equilibrium constant $0.02 \pm 0.003 \text{ M}$. We



suspect, however, that loss of a ligand from complex I, converting it from a di- to a monochelate, would be accompanied by a substantial change in λ_{max} and a much more pronounced diminution of absorbance than is observed. We therefore favor equilibrium 3, in which the dichelated structure is not disrupted.

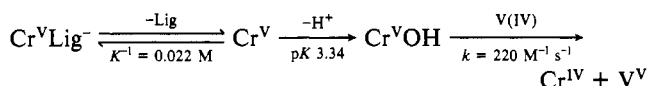
(30) Our kinetic data also allow a sequence in which the active reductant is a V(IV)-ligand complex from which one proton has been removed and the oxidants are dichelate I and form $(\text{Lig})_3\text{Cr}^V\text{O}$. Points in favor of such a formulation are (a) that the deprotonation of the V(IV)-ligand complex has been observed spectrophotometrically and (b) that attachment of a negative ligand to a reductant or removal of a proton, or both, commonly enhances its reactivity. Weighing against it are (a) that it implies different active reducing agents for the two stages of the reduction, (b) that it constitutes a reversal of the mechanism proposed³ for reduction of carboxylato-bound Cr(V) with Fe(II), and (c) that it allows no reasonable assignment of role for the slow (k_3) kinetic component.

(31) Deprotonation of $\text{VO}(\text{H}_2\text{O})_4^{2+}$ (pK_A 6.1) assumes importance only at pH values higher than those examined here. See, for example: Rossotti, F. J. C.; Rossotti, H. S. *Acta Chem. Scand.* **1955**, *9*, 1177.

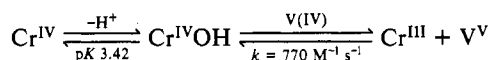
(32) Krumpolc, M.; Roček, J. *Inorg. Chem.* **1985**, *24*, 617.

from the fast (k_1') and slower (k_3') components may be considered reasonable in view of the many parameters generated by the two refinements. The slower conversion to Cr(IV) may then be represented:

Conversion to Cr(IV)



Reduction of Cr(IV)



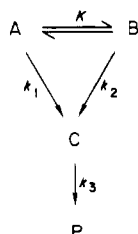
Following the overall reaction scheme, two different intermediate Cr(IV) species are expected to form initially if the ligand environments are same as those in their Cr(V) precursors, $(\text{Lig})_3\text{Cr}(\text{O})^-$ and the original dichelate I. A single kinetic component for reduction of this Cr(IV) suggests that the ligand-exchange reaction involving Cr(IV) is faster than the corresponding single reduction to form the Cr(III) product. If, as we believe, the Cr(III) product is the dichelate of the hydroxy carboxylic acid, the reactive Cr(IV) species may be taken to be a Cr(IV) dichelate.

Taking our kinetic scheme and the preexponential factors a , b , and c (see Appendix), we calculate the extinction coefficient of the Cr(IV) intermediate to fall between 1500 and 1900 $\text{M}^{-1} \text{ cm}^{-1}$. This range lies close to the value $1500 \pm 200 \text{ M}^{-1} \text{ cm}^{-1}$, reported for the analogous Cr(IV) intermediate as generated during the reaction between Fe(II) and Cr(V).⁵

An acceleration of the reduction of Cr(V) in the presence of added ligand is a common feature of all the three metal reductants, Ti(III), Fe(II), and V(IV). The detailed mechanistic implications may be different, however. For the first of these, since reduction is more rapid than substitution on Ti(III), an outer-sphere mechanism must predominate. The extra bound carboxyl ligand simply makes the Ti(III) complex a stronger reductant than $\text{Ti}(\text{H}_2\text{O})_6^{3+}$. In this Ti(III)-Cr(V) system, we saw no Cr(IV) although the reaction presumably proceeds through this state. Failure to detect such an intermediate implied that reduction of Cr(IV) by Ti(III) must be faster than the corresponding reduction of Cr(V), and a minimum rate ratio $k_{\text{Cr(IV)}}/k_{\text{Cr(V)}}$ was set at 20. In the Fe(II) reductions, the analogous ratio was very nearly unity at high ligand concentrations. According to the Marcus model of outer-sphere reactions³³ this rate ratio should very nearly be the same irrespective of reductants. On the basis of the latter ratio, and considering both the reductions of Cr(V) and Cr(IV) by Ti(III) to be outer sphere, the Fe(II) reduction of Cr(V) was proposed to be an inner-sphere process. The analogous rate ratios for the vanadium(IV) reduction of the extraligated Cr(V) and the dichelate I are 3.4 and 0.4, respectively. As in the Fe(II) reduction, the reductions of the two Cr(V) complexes by V(IV) appear to proceed mainly by inner-sphere mechanisms. However, the data now at hand do not allow such a choice between mechanisms for reduction of Cr(IV).

Appendix

Derivation of Eq 1. Consider a reaction scheme



(33) Marcus, R. A.: (a) *J. Phys. Chem.* **1963**, *67*, 853; (b) *Annu. Rev. Phys. Chem.* **1964**, *15*, 155.

in which the equilibrium $\text{A} \rightleftharpoons \text{B}$ is slow.

The concentrations of various species at any time t may be represented by

$$-d\text{A}/dt = k_1[\text{A}] \quad (\text{a})$$

$$-d\text{B}/dt = k_2[\text{B}] \quad (\text{b})$$

$$d\text{C}/dt = k_1[\text{A}] + k_2[\text{B}] - k_3[\text{C}] \quad (\text{c})$$

$$d\text{P}/dt = k_3[\text{C}] \quad (\text{d})$$

The initial equilibrium concentrations of the species A and B are $[\text{A}]_0$ and $[\text{B}]_0$. Moreover

$$[\text{A}]_{\text{T}} = [\text{A}]_0 + [\text{B}]_0 \quad (\text{e})$$

it then follows that

$$[\text{A}] = \frac{[\text{A}]_{\text{T}} e^{-k_1 t}}{1 + K} = k_1' [\text{A}]_{\text{T}} e^{-k_1 t} \quad (\text{f})$$

$$[\text{B}] = \frac{[\text{A}]_{\text{T}} K e^{-k_2 t}}{1 + K} = k_2' [\text{A}]_{\text{T}} e^{-k_2 t} \quad (\text{g})$$

where $k_1' = 1/(1 + K)$ and $k_2' = K/(1 + K)$. Combining eq f and g with eq c, and then rearranging, one obtains

$$d\text{C}/dt + k_3[\text{C}] = k_1' [\text{A}]_{\text{T}} e^{-k_1 t} + k_2' [\text{A}]_{\text{T}} e^{-k_2 t} \quad (\text{h})$$

Multiplying both sides by $e^{k_3 t}$ and integrating, one can write eq h as

$$\int_0^t d(e^{k_3 t} [\text{C}]) = k_1' [\text{A}]_{\text{T}} \int_0^t e^{(k_3 - k_1)t} + k_2' [\text{A}]_{\text{T}} \int_0^t e^{(k_3 - k_2)t} \quad (\text{i})$$

Integration generates

$$[\text{C}] = \frac{k_1' [\text{A}]_{\text{T}}}{k_3 - k_1} (e^{-k_1 t} - e^{-k_3 t}) + \frac{k_2' [\text{A}]_{\text{T}}}{k_3 - k_2} (e^{-k_2 t} - e^{-k_3 t}) \quad (\text{j})$$

Now

$$[\text{P}] = [\text{A}]_{\text{T}} - [\text{A}] - [\text{B}] - [\text{C}] \quad (\text{k})$$

Substituting the values of [A], [B], and [C] from eq f, g, and j, respectively, one obtains

$$\begin{aligned} [\text{P}] = & [\text{A}]_{\text{T}} - k_1' [\text{A}]_{\text{T}} e^{-k_1 t} \left(1 + \frac{1}{k_3 - k_1} \right) - \\ & k_2' [\text{A}]_{\text{T}} e^{-k_2 t} \left(1 + \frac{1}{k_3 - k_2} \right) + [\text{A}]_{\text{T}} e^{-k_3 t} \left(\frac{k_1'}{k_3 - k_1} + \frac{k_2'}{k_3 - k_2} \right) \quad (\text{l}) \end{aligned}$$

The absorbance of the system at any time t , D_t , is given by

$$D_t = \epsilon_{\text{A}}[\text{A}] + \epsilon_{\text{B}}[\text{B}] + \epsilon_{\text{C}}[\text{C}] + \epsilon_{\text{P}}[\text{P}] \quad (\text{m})$$

Substituting the values of [A], [B], [C], and [P] in eq m and representing $\epsilon_{\text{P}}[\text{A}]_{\text{T}} = D_{\infty}$, we find

$$D_t = a e^{-k_1 t} + b e^{-k_2 t} + c e^{-k_3 t} + D_{\infty} \quad (\text{n})$$

where

$$\begin{aligned} a = & k_1' \left\{ \epsilon_{\text{A}}[\text{A}]_{\text{T}} + \frac{\epsilon_{\text{C}}[\text{A}]_{\text{T}}}{k_3 - k_2} - D_{\infty} \left(1 + \frac{1}{k_3 - k_1} \right) \right\} \\ b = & k_2' \left\{ \epsilon_{\text{B}}[\text{A}]_{\text{T}} + \frac{\epsilon_{\text{C}}[\text{A}]_{\text{T}}}{k_3 - k_2} - D_{\infty} \left(1 + \frac{1}{k_3 - k_1} \right) \right\} \\ c = & D_{\infty} \left(\frac{k_1'}{k_3 - k_1} + \frac{k_2'}{k_3 - k_2} \right) - \frac{k_1' \epsilon_{\text{C}}[\text{A}]_{\text{T}}}{k_3 - k_1} - \frac{k_2' \epsilon_{\text{C}}[\text{A}]_{\text{T}}}{k_3 - k_2} \end{aligned}$$