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Electron Transfer. 50. Reduction of Carboxylato-Bound Chromium(V) with Hydrazine[1]

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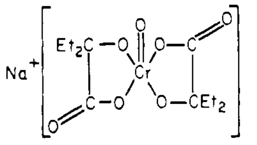
Solutions of the chromium(V) complex sodium bis(2-ethyl-2-hydroxybutyrato)oxochromate(V) (I) oxidize hydrazinium ion smoothly. Each mole of $N_2H_5^+$ consumes 2 mol of Cr(V), yielding N_2 and a Cr(III) product exhibiting ion-exchange behavior and an electronic spectrum consistent with a chelated monocarboxylato derivative of $(H_2O)_4Cr^{III}$. Kinetic results, obtained at pH 3.3–4.6 in the presence of added carboxylato ligand, point to a pair of two-electron transactions. The first of these, an oxidation to N_2H_2, is rate determining, whereas the second, the conversion to N_2, is rapid. Reactions, carried out in trimethylacetate buffers, are inverse first order in added 2-ethyl-2-hydroxybutyrate and are also inhibited by H^+. The algebraic form of the rate law (eq 3 in text) is consistent with a two-path mechanism (eq 5–9), both components of which involve preliminary rapid and reversible loss of a carboxylato ion from the Cr(V) oxidant. The resulting monocarboxylato intermediate then may undergo reduction either directly through (outer-sphere) reaction with $N_2H_5^+$ or, alternatively, via formation of a precursor complex, assembled with loss of H^+. The appearance of only one Cr(III) reaction product suggests that the Cr(V) species attacking N_2H_2 in the final rapid step(s) has the same ligand environment as that attacking $N_2H_5^+$ in the rate-determining steps.

The recent preparation, by Krumpolc and Roček,[3] of several water-soluble air-stable carboxylato derivatives of chromium(V) has added another transition-metal oxidation state to the group of redox centers deserving the attention of the experimentalist.[4,5] The present paper deals with the reduction, using hydrazine, of the Cr(V) complex sodium bis(2-ethyl-2-hydroxybutyrato)oxochromate(V) (I). We present evidence that alteration of ligation at the Cr(V) center precedes the acts of electron transfer in this reaction.



I

Experimental Section

Materials. Tris(hydroxymethyl)aminomethane ("Tris"), 2-ethyl-2-hydroxybutyric acid, and trimethylacetic acid (Aldrich products), hydrazinium hydrogen sulfate (Matheson, Coleman and Bell), and hydrazinium chloride (Alfa) were used as received. Lithium perchlorate was prepared as described.[6] Solutions of hydrazinium perchlorate were prepared either by careful neutralization of aqueous hydrazine (Matheson) with dilute $HClO_4$ or by conversion of the chloride with the use of an anion-exchange resin (AG2-X8, Bio-Rad, 200–400 mesh) in the perchlorate form. Hydrazine concentrations were estimated by titration with bromate as described by Kolthoff and co-workers.[7]

Sodium bis(2-ethyl-2-hydroxybutyrato)oxochromate(V) hydrate was prepared as described by Krumpolc.[3] Reliable kinetic results were obtained only with freshly prepared samples or material that had been purified by several reprecipitations from acetone–hexane shortly before use.

Anal. Calcd for $C_{12}H_{22}CrNaO_8$: C, 39.03; H, 6.01; Cr, 14.1. Found: C, 39.19; H, 5.99; Cr,[8] 14.6 (microanalyses by Galbraith Labs.)

Rate Measurements. Rates were estimated from measurements of decreases in absorbance at 510 nm, a Cr(V) absorption maximum,[3] with the use of a Beckman 5260 recording spectrophotometer. Ionic strengths were regulated with use of $LiClO_4$. All kinetic runs were carried out in the narrow pH range 3.3–4.6[9] since in our hands Cr(V) solutions having pH values outside this range suffered significant decomposition (disproportionation?) on the time scale of the hydrazine reaction. Reactions were unaffected by atmospheric O_2 or by addition of 0.01 M Mn^{2+} (as $MnSO_4$). Oxidations were first order each in Cr(V) and added hydrazine but were run under pseudo-first-order conditions with at least a fivefold excess of $N_2H_5^+$. Conversions were followed for at least 4 half-lives. Drifts in the infinity readings were slight and did not interfere seriously with kinetic analysis of the primary reaction. Rate constants from successive half-life values within a single run agreed to within 7%, and average values did not differ significantly from those obtained from logarithmic plots of absorbance differences against reaction times. Specific rates from replicate runs checked to better than 10%. Temperatures were kept at 25.0 ± 0.2 °C during the entire series of experiments.

Preliminary experiments with the methyl-substituted analogue of I, sodium bis(2-hydroxy-2-methylbutyrato)oxochromate(V),[3] indicated kinetic behavior parallel to that of the ethyl compound, with reduction rates about three times those of the latter compound; complications arising from secondary reactions were, however, more severe. Reactions of $N_2H_5^+$ with $Cr^{VI}(Na_2Cr_2O_7)$ were found to be less than one-twentieth as rapid as those with the ethyl-substituted Cr(V) complex I under corresponding conditions.

Stoichiometric Studies. The stoichiometry of the Cr^V–$N_2H_5^+$ reaction, with reductant in excess, was determined by adding a measured deficiency of the Cr(V) complex to the hydrazinium solution in 2.50 mL of aqueous trimethylacetate buffer, allowing 2 h for completion of the reaction (as indicated by the cessation of N_2 evolution), diluting the solution with 10 mL of concentrated HCl, adding 200 mg of KBr, and then titrating the unreacted hydrazine with standard $KBrO_3$ as described.[7] With oxidant in excess, stoichiometry was estimated from the decrease in absorbance at 510 nm, with the extinction coefficient of the Cr(V) complex and the Cr(III) product taken as 162 and 15 M^{-1} cm^{-1}, respectively. Representative results

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(2) On leave from Vivekananda College, Mylapore, Madras, India.

(3) M. Krumpolc and J. Roček, *J. Am. Chem. Soc.*, **101**, 3206 (1979).

(4) The literature is replete with instances in which Cr(V) is suggested as an intermediate in oxidations by Cr(VI) derivatives.[5] Until 1979, however, attempts to isolate and characterize water-soluble complexes of the pentavalent state were generally unsuccessful.

(5) See, for example: (a) F. H. Westheimer, *Chem. Rev.*, **45**, 419 (1949); (b) J. O. Edwards, *ibid.*, **50**, 455 (1952); (c) J. H. Espenson, *J. Am. Chem. Soc.*, **86**, 5101 (1964); (d) J. H. Espenson and E. L. King, *ibid.*, **85**, 3328 (1963); (e) K. G. Srinivasan and J. Roček, *ibid.*, **100**, 2729 (1978); (f) K. B. Wiberg, "Oxidation in Organic Chemistry", Part A, Academic Press, New York, 1965, pp 69–102.

(6) E. R. Dockal, E. T. Everhart, and E. S. Gould, *J. Am. Chem. Soc.*, **93**, 5661 (1971).

(7) I. M. Kolthoff, E. B. Sandell, E. J. Meehan, and B. Bruckenstein, "Quantitative Chemical Analysis", 4th ed., Macmillan, London, 1969, p 861.

(8) G. W. Haupt, *J. Res. Natl. Bur. Stand., Sect. A*, **48**, 414 (1952).

(9) Concentrations of trimethylacetic acid in the trimethylacetate buffers were below 0.03 M, reflecting the limited water solubility of this acid. The Cr^V–$N_2H_5^+$ reaction was found to be retarded by addition of acetate, but no dependence on trimethylacetate was observed.

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Table I. Stoichiometry of the Cr^V-$N_2H_5^+$ Reaction[a]

$[N_2H_5^+]$, M	$[Cr^V]$, M	$\Delta[N_2H_5^+]$	$\Delta[Cr^V]$	$\Delta[Cr^V]/\Delta[N_2H_5^+]$	medium
0.021	0.0138	0.00726[b]		1.90	0.02 M Me_3CCOOH + 0.02 M Me_3CCOO^-
0.021	0.0068	0.0035[b]		1.94	0.02 M Me_3CCOOH + 0.02 M Me_3CCOO^-
0.00112	0.0070		0.0022[c]	1.98	0.02 M Me_3CCOOH + 0.02 M Me_3CCOO^- + 0.0028 M ligand[d]
0.0064	0.0085		0.00136[c]	2.13	0.05 M tris·HCl
0.00160	0.0073		0.00310[c]	1.94	0.2 M HOAc + 0.2 M OAc^-

[a] $N_2H_5^+$ was added as hydrazinium bisulfate; Cr(V) was added as sodium bis(2-ethyl-2-hydroxybutyrato)oxochromate(V) (I). [b] Determined by titration with BrO_3^- in HCl (ref 7). [c] Determined spectrophotometrically at 510 nm (see Experimental Section). [d] 2-Ethyl-2-hydroxybutyric acid.

Table II. Representative Kinetic Data for the Reduction of Sodium Bis(2-ethyl-2-hydroxybutyrato)oxochromate(V) (I) with $N_2H_5ClO_4$[a]

$10^2 \times [N_2H_5^+]$, M	$10^4 \times [Cr^V]$,[b] M	$10^4 \times$ [HOLigH],[c] M	$10^4 \times [HOLig^-]$,[d] M	$10^4 \times [H^+]$,[d] M	$10^3 \times k_{obsd}$[e]	$10^3 \times k_{calcd}$[f]
2.3	5.3	7.5	5.8	1.40	2.8	2.9
4.6	5.3	7.5	5.8	1.40	5.9	5.7
6.9	5.3	7.5	5.8	1.40	9.0	8.8
11.6	5.3	7.5	5.8	1.40	14.5	14.8
11.6	10.6	7.5	5.8	1.40	15.3	14.8
11.6	5.3	16.7	13.1	1.40	6.9	6.6
11.6	5.3	33	26.1	1.40	3.2	3.3
11.6	5.3	84	66	1.40	1.57	1.30
11.6	5.3	167	131	1.40	0.78	0.65
11.6	5.5	11.4	5.8	4.8	7.8	8.3
11.6	5.5	9.4	5.8	3.1	9.9	10.3
11.6	5.5	8.4	5.8	2.2	11.0	11.9
11.6	5.5	7.9	5.8	1.82	12.9	13.1
11.6	5.5	6.9	5.8	0.96	15.4	17.1
11.6	5.5	6.5	5.8	0.55	19.9	20.6

[a] Reactions were carried out at 25 °C in 0.60 M $LiClO_4$. [b] Sodium bis(2-ethyl-2-hydroxybutyrato)oxochromate(V) (I). [c] 2-Ethyl-2-hydroxybutyric acid (total added). [d] Concentrations of H^+ and 2-ethyl-2-hydroxybutyrate ($HOLig^-$) were calculated by taking the pK_a of the parent acid as 3.32 and that of the buffer acid, trimethylacetic acid, as 4.54. These values were obtained by partial titrations of these acids at 24 °C in 0.60 M $LiClO_4$. [e] Pseudo-first-order rate constants (in s^{-1}) = $-d \ln [Cr^V]/dt$. [f] Calculated from rate law (3) in text with a taken as 1.48×10^{-4} s^{-1}, b as 0.183 M^{-1} s^{-1}, and c as 1.03×10^{-4} M.

are summarized in Table I. Very nearly 2.0 mol of Cr(V) react with each mole of hydrazine under the conditions specified. Note, however, that when Cr(V) is taken in only slight excess, increasing the time necessary for reaction, consumption of Cr(V) by secondary reaction(s) leads to marked apparent positive departures from 2:1 stoichiometry.

Solutions resulting from kinetic runs gave negative Nessler tests[10] for ammonia.

Examination of the Chromium(III) Products(s). A number of Cr^V–$N_2H_5^+$ reaction mixtures, 0.05 M in $N_2H_5ClO_4$ and 0.0017 M in Cr(V), each having a known concentration of added 2-ethyl-2-hydroxybutyrate, were allowed to react for 30 min, after which the mixtures were subjected to cation-exchange chromatography at 2 °C (Bio-Rad 50W-X2 sulfonate resin, Na^+ form, 200–400 mesh) as described.[11,12] Separations generally required about 60 min. In each case, the major portion of recovered Cr(III) was eluted with 0.1 M $NaClO_4$ and exhibited absorption maxima near 565 (ϵ 35 M^{-1} cm^{-1}) and 432 nm (ϵ 50). A second band, containing about 20% of the recovered chromium, showed characteristics (elution with 1.0–3.0 M $NaClO_4$: $\epsilon_{570\,nm}$ 13, ϵ_{406} 16) in accord with those of $Cr(H_2O)_6^{3+}$. The spectrum of the rapidly moving band corresponded to that of the Cr(III) reaction product measured without ion-exchange separation and, like the latter, was not altered by varying the concentration of carboxylato ligand added before reduction. However, recovery of chromium from the column was only partial (about 50%) and was substantially lowered further by a second passage. No improvement was achieved by using the resin in its H^+ form or by substituting a carboxylate resin (Rexyn 102(H)) for the sulfonate exchanger. Perceptible changes in the Cr(III) spectra resulted when the reduction was carried out with $N_2H_5^+Cl^-$ or $N_2H_5^+HSO_4^-$, rather than with the perchlorate; maxima for the chloride product (untreated with resin) were at 564 (ϵ 35) and 435 nm (ϵ 47), whereas those for the sulfate product were at 572 (ϵ 22) and 410 nm (ϵ 30).

Results and Discussion

Our stoichiometric studies indicate that, under a variety of conditions (Table I), 1 mol of $N_2H_5^+$ consumes 2 mol of Cr(V). This ratio, in conjunction with the absence of ammonia in the resulting reaction mixtures, allows us to represent the reaction in abbreviated form:

$$\text{hydrazine} + 2Cr^V \rightarrow N_2 + 2Cr^{III} \qquad (1)$$

but leaves unanswered questions as to the degree of protonation of the reactants and the ligand environment of the chromium species involved. The observed stoichiometry implies also that in the oxidation at hand, as in the reaction of hydrazine with the conventional two-electron oxidants IO_3^-, BrO_3^-, and Tl^{3+},[13] hydrazine is converted to N_2 by a pair of 2e transactions[14,15]

$$N_2H_4 \xrightarrow[-2H^+]{Cr^V} N_2H_2 \xrightarrow[-2H^+]{Cr^V} N_2 \qquad (2)$$

The straightforward exponential kinetic curves observed with $N_2H_5^+$ in excess indicate that the overall rate is determined by the initial step in the sequence of (2), i.e., that the oxidation of diimide, N_2H_2, is much more rapid than that of hydrazine.[16]

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(10) E. H. Swift, "A System of Chemical Analysis", Prentice-Hall, Englewood Cliffs, NJ, 1940, p 403.

(11) M.-Y. Wu, S. J. Paton, Y.-T. Fanchiang, E. Gelerinter, and E. S. Gould, *Inorg. Chem.*, **17**, 326 (1978).

(12) So that extinction coefficients for eluted Cr(III) species could be estimated, aliquots of each fraction were oxidized with basic H_2O_2 and the total chromium content determined as CrO_4^{2-}.[8]

(13) (a) W. C. E. Higginson, P. Sutton, and P. Wright, *J. Chem. Soc.*, 1380 (1953); (b) V. S. Srinivasan and N. Venkatasubramanian, *Indian J. Chem., Sect. A*, **15A**, 115 (1977).

(14) Reductions of Cr(VI) with hydrazine have also been found to give only N_2 as the oxidation product,[15] suggesting that although this oxidant can function as either a 1e or 2e reagent, each individual reaction step involving a chromium center and a nitrogen species is a 2e transaction.

(15) (a) M. T. Beck and D. A. Durham, *J. Inorg. Nucl. Chem.*, **32**, 1971 (1970); (b) V. M. Sadagopa Ramanujam and N. Venkatasubramanian, *Indian J. Chem.*, **8**, 948 (1970); (c) G. P. Haight, Jr., T. J. Huang, and H. Platt, *J. Am. Chem. Soc.*, **96**, 3137 (1974).

Our kinetic experiments therefore give no direct information concerning processes occurring after the first oxidation.

Representative kinetic data appear in Table II. Note that the redox reaction is retarded by increasing [H^+] or by addition of unbound carboxylato ligand. (The latter is here represented as $HOLig^-$ to differentiate it from the dinegative form, $OLig^{2-}$, bound to Cr(V) in the chelated starting material.) In the presence of added ligand and within the ranges of concentrations indicated in Table II, reaction rates conform to relationship (3). An iterative nonlinear least-squares refinement,

$$\text{rate} = \frac{[N_2H_5^+][Cr^V]}{[HOLig^-]}\,\frac{a + b[H^+]}{1 + [H^+]/c} \qquad (3)$$

minimizing the function $(k_{obsd} - k_{calcd})^2$ (where the k's represent pseudo-first-order rate constants, $-d \ln [Cr^V]/dt$, with $N_2H_5^+$ in excess), yielded the following parameters: $a = (1.48 \pm 0.17) \times 10^{-4}$ s^{-1}; $b = 0.183 \pm 0.080$ M^{-1} s^{-1}; $c = (1.03 \pm 0.40) \times 10^{-4}$ M.[17] Table II also compares observed rates with those calculated with the use of (3).

The rate law of (3) implies two reaction paths. In each, the transition state leading to the rate-determining step consists of a hydrazine species, a Cr(V) center from which one carboxylato ligand has been separated, and an unknown number of water molecules. The simplest sequence in accord with (3) features a pair of activated complexes at different protonation levels, both derived from a Cr(V) complex which has lost one ligand in a preliminary equilibrium. This sequence leads to the rate law (4) where k_A and k_{HA} indicate specific rates

$$\text{rate} = \frac{[N_2H_5^+][Cr^V]}{[HOLig^-]}\,\frac{k_A K_{HA} + k_{HA}[H^+]}{K_{HA} + [H^+]} \qquad (4)$$

associated with the deprotonated and protonated paths and K_{HA} is the acidity constant of the species undergoing partial deprotonation in the system at hand. Equation 4 is equivalent algebraically to the empirical expression (3), with a calculated pK_{HA} (=$-$log c) of 4.0 ± 0.2. The sequence from which it is derived is therefore open to objection since neither hydrazine (for which pK_{HA} values of 8.07[18a] and $-$0.88[18b] have been reported) nor the Cr(V) complex (the spectrum of which has been found to be invariant between pH 3.3 and 4.3)[19] exhibits an appropriate pK_{HA}.

We favor instead a two-path sequence in which the major portion of the reaction proceeds through a Cr^V–hydrazine precursor complex (P), formed reversibly with expulsion of H^+, with a minor fraction bypassing this precursor, presumably reacting by an outer-sphere route (k_{OS}). Both paths appear to be initiated by loss of ligand $HOLig^-$ from a diligated species, very likely the hydrated form, $(OLig^{2-})_2Cr(O)(OH_2)^-$, of the original Cr(V) chelate.[20] (The sequence is illustrated in eq 5–9.) Application of the steady-state approximation

$$\underset{\text{“}Cr^VL_2\text{”}}{(OLig^{2-})_2Cr(O)(OH)_2} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (OLig^{2-})Cr(O)(OH) + HOLig^- \qquad (5)$$

$$(OLig^{2-})Cr(O)(OH) + N_2H_5^+ \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \underset{\text{“P”}}{(OLig^{2-})Cr(O)N_2H_4(OH)} + H^+ \qquad (6)$$

$$P \xrightarrow{k_3} (HOLig^-)Cr^{III}(OH)_2 + N_2H_2 \qquad (7)$$

$$(OLig^{2-})Cr(O)(OH) + N_2H_5^+ \xrightarrow{k_{OS}} (HOLig^-)Cr^{III}(OH)(H_2O^+) + N_2H_2 \qquad (8)$$

$$N_2H_2 + (OLig^{2-})Cr(O)(OH) \xrightarrow{\text{rapid}} N_2 + (HOLig^-)Cr(OH)_2 \qquad (9)$$

to the precursor, P,, and to the monocarboxylato intermediate $(OLig^{2-})Cr(O)OH$ leads us to the rate expression (10).

$$\text{rate} = \frac{k_1[Cr^VL_2][N_2H_5^+]}{\dfrac{k_2k_3[N_2H_5^+]}{k_{-2}[H^+] + k_3} + k_{-1}[HOLig^-]}\left[\frac{k_2k_3}{k_{-2}[H^+] + k_3} + k_{OS}\right] \qquad (10)$$

Moreover, if the $k_{-1}[HOLig^-]$ term in the denominator of (10) is taken to be much greater than the k_2k_3 term, this expression may be simplified to (11) which is likewise analogous to the

$$\text{rate} = \frac{[Cr^VL_2][N_2H_5^+]}{[HOLig^-]}\,\frac{\dfrac{k_1}{k_{-1}}(k_{OS} + k_2) + \dfrac{k_1k_{-2}k_{OS}}{k_{-1}k_3}[H^+]}{1 + \dfrac{k_{-2}}{k_3}[H^+]} \qquad (11)$$

observed rate law, (3). According to this view, the empirical parameters a, b, and c are functions of the rate constants for the several individual steps, constants that cannot be evaluated from steady-state experiments alone. We further suspect that the two electrons transferred in (7) are those constituting the Cr–N bond in precursor P and that the oxidized nitrogen species is thus free to depart after the transfer act despite the recognized substitution-inert character of Cr(III). The proposed sequence is not unlike that favored by Haight and coworkers[15c] for oxidation of $N_2H_5^+$ by Cr(VI) at high acidities.

Our observations concerning the Cr(III) product appear to be in accord with the suggested mechanism. The visible spectrum of this product, which features maxima at 565 (ϵ 35) and 432 nm (ϵ 50), points to a chelated monocarboxylato $(H_2O)_4Cr^{III}$ species,[21] and its elution behavior is consistent with that of a dipositive ion.[22,23] Since we find no evidence for

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(16) A proposed alternative sequence,[15c] featuring the rapid disproportionation of N_2H_2 to N_2 and N_2H_4, appears to be much less likely for our systems in view of the very low concentration of this intermediate and the demonstrably slow disproportionation of diimide at substrate concentrations in the gas phase near room temperature. See, for example, C. Willis and R. A. Back, *Can. J. Chem.*, **51**, 3605 (1973).

(17) The relatively large uncertainties in the derived parameters b and c reflect the circumstance that rates are not highly sensitive to [H^+], i.e., that they are determined in large part by [$N_2H_5^+$], [Cr^V], and [$HOLig^-$].

(18) (a) R. L. Hinman, *J. Org. Chem.*, **23**, 1587 (1958) (this value (for $N_2H_5^+$) was determined at 30 °C); (b) G., Schwarzenbach, *Helv. Chim. Acta*, **19**, 178 (1936); this (highly approximate) value applies to $N_2H_6^{2+}$.

(19) Attempted determinations of pK_a's for (carboxylato)chromium(V) complexes by partial acidimetric titration have encountered the difficulty that these derivatives undergo decomposition in water at pH values >4.6 in the absence of excess ligand, yielding Cr(III), $HCrO_4^-$, and the parent carboxylic acid, each of which reacts with added base.

(20) A number of chelated carboxylato derivatives of Cr(V), including the complex used in the present study, have been reported[3] to exhibit a strong affinity for an additional water molecule, even when prepared in the crystalline state.

(21) See, for example, A. Liang and E. S. Gould, *J. Am. Chem. Soc.*, **92**, 6791 (1970). These authors report pK_A for the dipositive chelated salicylato derivative of $(H_2O)_4Cr^{III}$ as 0.5. Since the ligands in the present system feature alcoholic rather than phenolic OH groups, pK_A for the analogous dipositive chelates should be several units greater than this. We therefore represent these Cr(III) chelates in their dipositive forms, i.e., as hydroxycarboxylato derivatives, in contrast to the Cr(V) chelates, which are oxycarboxylato derivatives, reflecting the acid-strengthening action of the Cr(V) center.

(22) Interpretation of our ion-exchange experiments is complicated somewhat by the partial hydrolysis and polymerization of the principal Cr(III) product on the resins used, processes which have been reported for a variety of (carboxylato)chromium(III) cations.[23] Since the principal recovered species has virtually the same spectrum as that of the unseparated product, we infer that the $Cr(H_2O)_6^{3+}$ eluted arises from hydrolysis rather than separation of the reduction product into two components (one of which should exhibit ϵ values greater than those of the unseparated product). Note also that these studies do not preclude the formation of a minor quantity of a nonchelated carboxylato product.

comparable amounts of two such products, we infer that the oxidizing species attacking N_2H_2 (or $N_2H_3^+$) in the final rapid step (9) has the same ligand environment as that attacking $N_2H_5^+$ in the rate-determining steps.

One point continues to concern us. The proposed mechanism includes a dissociation equilibrium involving departure of the ligand $HOLig^-$ from the Cr^V center and its return, with the rate constants for forward (k_1) and reverse (k_{-1}) components much greater than that for the subsequent formation of the precursor complex, P (k_2). Even if it is assumed that the labile carboxyl is attached to Cr(V) through only one donor site (i.e., $-COO^-$), the implication is that both formation and breakage of a Cr^V–O bond are much more rapid than formation of a Cr^V–N bond. Such a conclusion would appear to be inadmissible if applied to octahedral complexes of the first-row transition-metal ions in their +2 and +3 states, for these undergo substitution by variants of a dissociative process with rates determined, in large part, by the metal–ligand bond being broken rather than by the bond formed.[24] The story is much less clear for substitution reactions at centers derived from metals in very high oxidation states (e.g., Ti(IV), V(V), Cr(V), and Cr(VI)). Here, nonoctahedral geometries, angular distortion of coordination polyhedra, and unusually strong polarization of the metal–ligand bonds complicate the picture, and broad mechanistic generalizations have not yet emerged.[25] However, rates of substitution at Cr(VI) have been shown to be highly sensitive to the structure of the attacking nucleophile,[26] and it would not be astonishing to find an analogous sensitivity for reactions of the pentapositive state as well.

Appendix

Derivation of Equations 10. The steady-state equations applied to the precursor, P, and the monocarboxylato intermediate $(OLig^{2-})Cr(O)OH$ (abbreviated CrCl below) in the sequence (5)–(7) are

$$d[CrL]/dt = 0 = k_1[CrL_2] - k_{-1}[CrL][L^-] - k_2[CrL][N_2H_5^+] + k_{-2}[P][H^+] \quad (a)$$

$$d[P]/dt = 0 = k_2[CrL][N_2H_5^+] - k_{-2}[P][H^+] - k_3[P] \quad (b)$$

Addition of (a) and (b) and then rearranging give (c) whereas

$$[P] = (k_1[CrL_2] - k_{-1}[CrL][L^-])/k_3 \quad (c)$$

simple rearrangement of (b) gives (d). Equating (c) and (d)

$$[P] = k_2[CrL][N_2H_5^+]/(k_{-2}[H^+] + k_3) \quad (d)$$

and then solving for [CrL] lead to (e). The proposed two-path

$$[CrL] = \frac{k_1[CrL_2]}{\dfrac{k_2k_3[N_2H_5^+]}{k_{-2}[H^+] + k_3} + k_{-1}[L^-]} \quad (e)$$

reaction sequence implies the rate expression (f). Substitution

$$\text{rate} = k_3[P] + k_{OS}[CrL][N_2H_5^+] \quad (f)$$

of (d) and (e) into (f) and then rearranging give equation 10 in the text.

Registry No. I, 70132-29-5; $N_2H_5^+$, 18500-32-8.

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(23) E. S. Gould, *J. Am. Chem. Soc.*, **90**, 1740 (1968).

(24) See, for example, F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions", 2nd ed., Wiley, New York, 1967, Chapter 3.

(25) See, however: (a) A. Lifshitz and B. Perlmutter-Hayman, *J. Phys. Chem.*, **65**, 2098 (1961); **69**, 1736 (1965); (b) H. Weingarten and J. R. Van Wazer, *J. Am. Chem. Soc.*, **88**, 2700 (1966).

(26) P. Moore, S. F. A. Kettle, and R. G. Wilkins, *Inorg. Chem.*, **5**, 220 (1966).

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Asymmetric Induction on Decarboxylation of α-Amino-α-alkylmalonic Acids Chelated to Chiral Cobalt(III) Complexes

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The Λ-β_2-[Co(α-amino-α-alkylmalonato)(N_4)]$^+$ complexes, where α-amino-α-alkylmalonato = α-amino-α-methylmalonato (AMM), α-amino-α-isopropylmalonato (AIPM), α-amino-α-benzylmalonato (ABzM), and α-amino-α-isobutylmalonato (AIBM) and N_4 = chiral derivatives of 3,7-diazanonane-1,9-diamine (2,3,2-tet) and triethylenetetramine (trien), were prepared from *trans*-[$CoCl_2(N_4)$]$^+$. The chelated α-amino-α-alkylmalonate stereospecifically took the *R* configuration. Decarboxylations of the α-amino-α-alkylmalonato complexes in acidic aqueous or methanolic solution gave rise to a diastereomeric mixture of the corresponding (*R*)- and (*S*)-amino acidato complexes (Λ-*R* and Λ-*S* isomers). Considerable asymmetric induction was observed. In the most favorable case, the formation ratio (Λ-*S*/Λ-*R*) on decarboxylation was 2/98 of the AIPM complex with N_4 = 1,7-bis(2(*S*)-pyrrolidyl)-2,6-diazaheptane (abbreviated as *SS*-pyht).

Introduction

α-Amino-α-alkylmalonic acids are useful intermediary compounds for syntheses of a variety of α-amino acids.[1] α-Amino-α-alkylmalonic acids have a prochiral center since it contains two enantiotopic carboxyl groups. Asperger and Liu[2] reported that α-amino-α-methylmalonic acid ($AMMH_2$) coordinated to a chiral cobalt(III) complex with its amino and one of the carboxylate groups decarboxylated (at pH 7.5–8.0) yielded stereoselectively the corresponding (*S*)-alaninato complex and that the alanine liberated from the decarboxylated complex showed a 14% excess of (*S*)-alanine over (*R*)-alanine, even though the decarboxylation product seemed to be the

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(1) Greenstein, J. P.; Winitz, M. "Chemistry of the Amino Acids"; Wiley: New York, 1961; Vol. 3

(2) Asperger, R. G.; Liu, C. F. *Inorg. Chem.* **1967**, *6*, 796.

(3) The abbreviation for this tetraamine, L,L-α,α′-dimethyltrien, used by Asperger and Liu[2] is not appropriate because the positions of the substituents are not clearly indicated. The tetraamine is newly abbreviated according to the system shown in Table I.

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