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Electron Transfer through Organic Structures. 29. A Reversed Acidity Pattern in Carboxylato-Bridged Reductions by Vanadium(II)[1]

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The reductions of several (di- and (trialkylacetato)pentaamminecobalt(III) complexes with V^{2+} (25 °C, $\mu = 4.0$) are accelerated as $[H^+]$ is increased from 0.10 to 4.0 M, a reversal of the acidity pattern ordinarily observed for reactions of this type. After correction of the trialkyl, but not the dialkyl, derivatives for kinetic medium effects, the reductions conform to a rate law (eq 1) pointing to partition of the cobalt into a nonprotonated and a more rapidly reacting protonated form. The observed reversal arises because the increased branching at the α carbon of the carboxyl ligand has depressed the specific rate of the nonprotonated bridged component below that of the protonated outer-sphere path (which is much less sensitive to nonbonded interactions). Acidity constants for the protonated forms of the oxidants have been evaluated, as have specific rates for the two forms of each oxidant. The acidities of the branched oxidants are found to lie above those for the straight-chain acetato and propionato complexes, probably reflecting the greater difficulty in solvating the protonated (tripositive) forms bearing bulky lipophilic groups.

Although the mediating action by carboxyl ligands on the inner-sphere reductions of bound cobalt(III) can be significantly altered by protonation,[2] the resulting dependencies are at present inadequately understood. In particular, when the basic site is conjugated with $COOCo^{III}$ but lies out of the path of electron transfer, protonation may increase[3] or decrease[4] the rate of reduction, but the electronic features which govern the direction of the effect have not been defined. In cases where electron transfer occurs through an extended segment of the ligand (remote attack), protonation often accelerates the reaction,[5] but, again, no convincing rationale for this rate enhancement has yet appeared. The picture is more straightforward for reactions proceeding through chelated transition states, for here protonation simply ties off a basic site in the oxidant where chelation might otherwise occur.[6] Finally, when the lead-in function constitutes the only basic site in the bridging ligand, attachment of H^+ blocks off the bridged path, leaving only an outer-sphere route for the protonated oxidant.

The latter description applies to the reductions, using Cr^{2+}, Eu^{2+}, and V^{2+}, of the acetato and propionato derivatives of $(NH_3)_5Co^{III}$, each of which is strongly retarded at high acidities. Earlier studies[7,8] yielded values for the acidity constants of these oxidants and indicated that the ratio of specific rates, k_V/k_{Eu}, associated with reductions of the protonated forms, corresponds closely to the ratios observed for known outer-sphere series.[9] It was further suggested that since the inner-sphere path is much more sensitive than the outer-sphere to the degree of alkylation in the carboxyl group,[9] it should be possible, by increasing branching, to depress the specific rate of the bridged component below that of the protonated outer-sphere path. In such instances, protonation would accelerate, rather than retard, reaction, and a reversal of the usual acidity pattern for this type of system would result. We here report several examples of such an inversion.

Experimental Section

Materials. Solutions of V(II) were prepared and analyzed as described.[10] Cobalt complexes not available from previous studies[9,11] were prepared by known methods.[9,12] Lithium perchlorate was prepared as described.[13] Ligands (Aldrich, K&K, or Pfaltz and Bauer products) were used without purification.

Rate Measurements. Rates were estimated from measurements of absorbance decreases on the Cary 14 spectrophotometer as described.[7,10a,11] Measurements were made at 502 nm. Reactions were first order each in Co(III) and V^{2+}, but rate measurements were carried out under pseudo-first-order conditions with at least a tenfold excess of V^{2+}. Ionic strengths were adjusted using twice-recrystallized $LiClO_4$. To minimize volume changes resulting from mixing reagents, the solution containing $V(ClO_4)_2$, perchloric acid, and lithium perchlorate was made up to the appropriate volume, and a known volume of a concentrated solution of the Co(III) complex was added using a small calibrated syringe. Reactions were followed for at least 5 half-lives. Rate constants evaluated from successive half-life values within a single run generally agreed to within 3%. Except as noted below, no trends indicative of systematic errors were observed, and average values did not differ significantly from those obtained from least-squares treatment of logarithmic plots of absorbance differences against reaction time. Specific rates obtained from replicate runs checked to within 5%. Temperatures were kept at 25.0 ± 0.2 °C during the entire series of experiments.

The V(II) reductions of the chloroacetato, trichloroacetato, and heptafluorobutyrato complexes of $(NH_3)_5Co^{III}$ did not give simple kinetic curves. Stoichiometry studies[12] indicated that reductions of the chlorinated complexes were complicated by competing reduction of bound chlorine in a manner analogous to that described for Cr^{2+} reductions.[7] The source of difficulty with the fluorinated derivative is less clear, but we suspect that this complex undergoes significant aquation, as well as reduction, in the reaction media employed.

Results and Discussion

Kinetic data for reductions at various acidities appear in Tables I–III. The rates listed in Table I are independent of acidity or exhibit a dependence which is too slight to be ki-

Table I. Specific Rates of Vanadium(II) Reductions of Various (Carboxylato)pentaamminecobalt(III) Complexes ($\mathrm{RCo(NH_3)_5}^{2+}$)

Ligand, R	μ	$[\mathrm{H}^+]$, M	k[a]
Aquo	4.0	0.5	1.47
		1.0	1.45
		2.5	1.45
		3.5	1.44
		4.0	1.46
Methylmalonato	4.0	0.5	11.4
		4.0	11.4
Dimethylmalonato	4.0	0.5	5.7
		4.0	5.7
1,1-Cyclobutanedicarboxylato	4.0	0.5	8.0
		4.0	8.0
	1.0	0.1	1.38
		1.0	1.34
Malonato	1.0	0.1	6.2
		0.3	6.0
		1.0	6.1
Salicylato	1.0	0.1	1.13
		1.0	1.15
Pyruvato	1.0	0.1	10.2
		1.0	10.8
Diphenylacetato	4.0	0.5	1.49
		1.0	1.37
		2.0	1.33
		3.0	1.28
		4.0	1.17
Benzylglycolato	4.0	0.5	6.3
		4.0	5.5

[a] Specific rates in $\mathrm{M^{-1}\ s^{-1}}$ at 25 °C. Supporting electrolyte is $\mathrm{LiClO_4}$. In most cases, values are averages of two to four replicate runs. Agreement between runs was better than 5%.

Table II. Kinetic Data for Vanadium(II) Reductions of (Diethylacetato)- and (Di-*n*-propylacetato)pentaamminecobalt(III) Complexes[a]

	$[\mathrm{H}^+]$, M	k_{obsd}[b]	k_{calcd}[c]
Diethyl	0.10	0.84	0.838
	0.30	1.00	0.977
	0.50	1.04	1.078
	0.70	1.13	1.156
	1.00	1.29	1.244
	1.50	1.31	1.344
	2.00	1.46	1.410
	2.50	1.46	1.458
	3.50	1.50	1.521
	4.00	1.54	1.543
Dipropyl	0.10	0.71	0.703
	0.30	0.80	0.783
	0.50	0.82	0.846
	0.70	0.87	0.897
	1.00	0.96	0.957
	1.50	1.03	1.029
	2.00	1.13	1.079
	2.50	1.13	1.116
	3.00	1.13	1.145
	3.50	1.13	1.168
	4.00	1.19	1.186

[a] Specific rates in $\mathrm{M^{-1}\ s^{-1}}$ at 25 °C; $\mu = 4.0$, supporting electrolyte $\mathrm{LiClO_4}$. $[\mathrm{Co^{III}}]_0 = 0.0003\text{–}0.003$ M; $[\mathrm{V}^{2+}] = 0.003\text{–}0.03$ M. Most values are averages of two to four replicate runs with agreement between runs better than 5%. [b] k_{obsd} defined as $(-d[\mathrm{Co^{III}}]/dt)[\mathrm{Co^{III}}]^{-1}[\mathrm{V}^{2+}]^{-1}$. [c] k_{calcd} from eq 1, using parameters listed in Table IV.

Table III. Kinetic Data for Vanadium(II) Reductions of (Trimethyl- and (Triethylacetato)pentaamminecobalt(III)) Complexes[a]

	$[\mathrm{H}^+]$, M	k_{obsd}	k_{calcd}[b]
Trimethyl	0.10	0.51	0.509
	0.20	0.53	0.531
	0.30	0.55	0.551
	0.50	0.59	0.585
	1.00	0.66	0.653
	1.50	0.69	0.707
	2.00	0.77	0.755
	2.50	0.80	0.800
	3.00	0.84	0.842
	3.50	0.88	0.884
	4.00	0.93	0.927
Triethyl	0.10	0.38	0.382
	0.30	0.42	0.422
	0.50	0.46	0.457
	0.70	0.49	0.489
	1.00	0.53	0.533
	1.50	0.60	0.602
	2.00	0.67	0.670
	2.50	0.69[c]	0.738
	3.00	0.81	0.808
	3.50	0.88	0.881
	4.00	0.88[c]	0.954

[a] Specific rates in $\mathrm{M^{-1}\ s^{-1}}$ at 25 °C; $\mu = 4.0$; supporting electrolyte $\mathrm{LiClO_4}$. Reaction conditions are similar to those listed in Table II. [b] k_{calcd} from eq 2, using parameters in Table IV. [c] Excluded from final cycle of least-squares refinement.

netically meaningful at our level of precision. Each of the carboxylato complexes in this group features an electron attracting group (a second carboxyl or a benzene ring) and may be presumed not to undergo further protonation in the acidity range studied.[14,15] These data, which are analogous to the Cr^{2+} results of Lavallee and Deutsch,[16] indicate that kinetic medium effects arising from substitution of Li^+ for H^+ in aqueous perchlorate media are slight for reactions of this type but are not necessarily negligible, particularly when the ligand bears one or more large lipophilic substituents.

Specific rates for the dialkylacetato complexes (Table II) and the related trialkyl derivatives (Table III) are seen to rise with acidity, a trend which might reflect a true kinetic effect, medium effects, or a combination of the two. If the observed increases result solely from protonation of the oxidant, rates should conform to eq 1[7,8] in which the specific rates k_{A} and

$$\text{rate} = [\mathrm{Co^{III}}]\,[\mathrm{V^{II}}]\frac{k_{\mathrm{A}}K_{\mathrm{HA}} + k_{\mathrm{HA}}[\mathrm{H}^+]}{K_{\mathrm{HA}} + [\mathrm{H}^+]} \qquad (1)$$

k_{HA} refer to the nonprotonated and protonated forms of the oxidant, and K_{HA} is the acidity constant for the protonated oxidant. On the other hand, if only medium effects are operative, the fraction in (1) is replaced by the exponential term $e^{\beta[\mathrm{H}^+]}$,[17] where β, a kinetic medium parameter, representing the response of the reaction at hand to replacement of Li^+ for H^+ in the supporting electrolyte, may be positive or negative. The more complicated relationship in eq 2 describes a su-

$$\text{rate} = [\mathrm{Co^{III}}]\,[\mathrm{V^{II}}]\frac{k_{\mathrm{A}}K_{\mathrm{HA}} + k_{\mathrm{HA}}[\mathrm{H}^+]}{K_{\mathrm{HA}} + [\mathrm{H}^+]}\,e^{\beta[\mathrm{H}^+]} \qquad (2)$$

perposition of both effects. Although distinction between these possibilities is difficult when the variation in the medium is narrow, plots of log k_{obsd} vs. $[\mathrm{H}^+]$ for all four oxidants are strongly curved in the region $[\mathrm{H}^+] = 0.1\text{–}1.5$ M (indicating protonation in this range), whereas medium effects alone would result in a linear relationship. Moreover, for the dialkyl complexes such plots become very nearly horizontal at high acidities, pointing to a vanishingly small value of β for these oxidants.

With the aid of iterative nonlinear least-squares procedure, we have applied eq 1 to our dialkyl and eq 2 to our trialkyl systems. Values of k_{A}, k_{HA}, K_{HA}, and β giving the closest fit to the observed rates have been obtained.[18,19] These appear in Table IV, along with earlier parameters for the acetato and propionato complexes.[8] Rates calculated using these parameters are compared to the observed rates in Tables II and III.

Table IV. Calculated Kinetic Parameters for the Vanadium(II) Reductions of Substituted (Acetato)pentaamminecobalt(III) Complexes ($RCo(NH_3)_5{}^{2+}$)[a]

Ligand, R	K_{HA}, M	k_A	k_{HA}	β, M^{-1} [b]
Diethylacetato	1.0 ± 0.2	0.74 ± 0.05	1.74 ± 0.06	
Di-*n*-propylacetato	1.3 ± 0.4	0.65 ± 0.04	1.37 ± 0.06	
Trimethylacetato	1.1 ± 0.7	0.48 ± 0.01	0.74 ± 0.10	0.075 ± 0.020
Triethylacetato	1.2 ± 0.3	0.36 ± 0.01	0.59 ± 0.04	0.147 ± 0.009
Acetato[c]	0.35 ± 0.07[d] 0.48 ± 0.11[e]	3.15 ± 0.12	1.22 ± 0.03	
Propionato[c]	0.24 ± 0.04[d]	2.66 ± 0.10	1.30 ± 0.02	

[a] Reactions at 25 °C, $\mu = 4.0$. Specific rates, in $M^{-1}\ s^{-1}$, calculated by minimization of the function $(k_{calcd} - k_{obsd})^2$, where values of k_{calcd} for the dialkyl derivatives are obtained from eq 1 and those for the trialkyl complexes are obtained from eq 2 (see text). [b] Kinetic medium parameter, defined in eq 2. [c] See ref 8. [d] Obtained from kinetic data for reductions with Cr^{2+}, V^{2+}, and Eu^{2+}. [e] Spectrophotometric value (see ref 7).

Aside from the trimethylacetato complex, the K_{HA} value of which is highly uncertain, the acidities of the branched complexes in the present study are seen to lie substantially above those of the straight chain acetato and propionato complexes, in contrast to the trend observed for the parent carboxylic acids, in which α-alkylation generally decreases acidity.[20] Note, however, that the complexes in our study are more strongly solvated in their protonated (tripositive) than in their nonprotonated (dipositive) forms, whereas the reverse is true for the uncoordinated acids. Hence, it is not astonishing that the presence of bulky groups, which make solvation more difficult, should affect the two types of equilibrium in opposite directions.

The trend in k_A values is unexceptional and serves merely as a reminder that carboxylato-bridged reductions by V^{2+} are sensitive (although less markedly so than those by Cr^{2+})[9] to nonbonded interactions between the side chain and the reductant. Variations in the outer-sphere protonated component, k_{HA}, are slight and almost random, in accord with the view[20] that the degree of electron withdrawal from the coordinated carboxyl, to which outer-sphere reduction rates are known to be sensitive,[9,21] is scarcely affected by variation in alkyl substitution at the α carbon.

It is anticipated that the reverse acidity pattern described here for V^{2+} applies also to the reductions of the triethylacetato complex by Eu^{2+} and Cr^{2+}, for with both of these reductants k_{HA} very probably lies significantly above k_A.[22] Experimental verification, however, is likely to be less straightforward in the case of these more slowly reacting systems, for at the high concentrations of electrolyte which must be used, aquation of the oxidant may seriously compete with electron transfer.

Registry No. V^{2+}, 15121-26-3; (aquo)$Co(NH_3)_5{}^{2+}$, 14403-82-8; (methylmalonato)$Co(NH_3)_5{}^{2+}$, 63950-83-4; (dimethylmalonato)$Co(NH_3)_5{}^{2+}$, 38897-91-5; (1,1-cyclobutanedicarboxylato)$Co(NH_3)_5{}^{2+}$, 50578-38-6; (malonato)$Co(NH_3)_5{}^{2+}$, 38897-90-4; (salicylato)$Co(NH_3)_5{}^{2+}$, 30931-74-9; (pyruvato)$Co(NH_3)_5{}^{2+}$, 19306-91-3; (diphenylacetato)$Co(NH_3)_5{}^{2+}$, 47197-62-6; (benzylglycolato)$Co(NH_3)_5{}^{2+}$, 51965-56-1; (diethylacetato)$Co(NH_3)_5{}^{2+}$, 51965-53-8; (dipropylacetato)$Co(NH_3)_5{}^{2+}$, 51965-52-7; (trimethylacetato)$Co(NH_3)_5{}^{2+}$, 33887-25-1; (triethylacetato)$Co(NH_3)_5{}^{2+}$, 51965-36-7; H^+, 12408-02-5.

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(18) For convergence in the least-squares refinement procedures, it is necessary that the trial values of the parameters used initially be reasonably close to the ultimate refined values. Procedures for preliminary estimates of k_{HA}, k_A, and K_{HA} have been described.[8] Trial values of β for the trialkyl refinements may be obtained from the slopes of plots of ln k_{obsd} vs. $[H^+]$ in the region $[H^+]$ = 2.5–4.0 M. No significant improvement of fit resulted from application of eq 2, rather than eq 1, to the dialkylated oxidants.

(19) Kinetic medium parameters (β values) calculated for the trialkylated oxidants are of opposite sign from that reported by Toppen and Linck[17b] for the Cr^{2+} reduction of $(NH_3)_5CoH_2O^{3+}$ at 25 °C. We cannot say whether this reversal is associated with the change in reducing agent or with the ligation of a large lipophilic substituent to the oxidizing center. Comparably puzzling is the appearance of this medium effect only when the third alkyl group has been attached, suggesting that the solvent-orienting abilities of Li^+ and H^+, although very similar in highly polar media, may diverge significantly in the vicinity of a precursor complex in which the reaction center is protected in virtually all directions by alkylation.

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