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Kinetics and Mechanisms of the Reductions of μ -(Carboxyacetylenecarboxylato-*O,O'*)-di- μ -hydroxo-bis[triamminecobalt(III)] and Its μ -(Fumarato-*O,O'*) Analogue by Vanadium(II)

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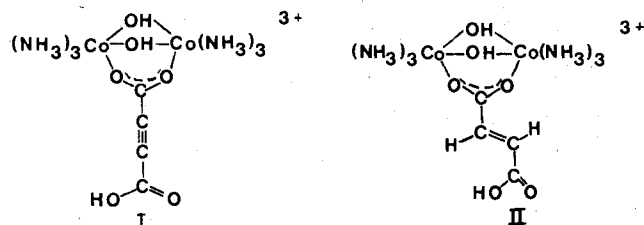
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The kinetics of the reductions of μ -(carboxyacetylenecarboxylato-*O,O'*)-di- μ -hydroxo-bis[triamminecobalt(III)] and its μ -(fumarato-*O,O'*) analogue by $[V(OH_2)_6]^{2+}$ in perchloric acid media have been studied. Reduction of the first cobalt(III) ion is rate determining in both cases. The reductions are dependent on H^+ concentration. It is proposed that the protonated and deprotonated forms of complexes I and II react with V(II) at different rates to form products. From differing activation parameters it is concluded that the protonated forms of both complexes are reduced by outer-sphere mechanisms whereas the deprotonated forms react by inner-sphere mechanisms with substitution of the remote uncomplexed carboxylic group into $[V(OH_2)_6]^{2+}$ being the rate-determining step followed by transfer of an electron through a C=C or C≡C bond.

Introduction

Electron transfer through extended organic structural units appears to be a less common reaction path for reductions with $[V(OH_2)_6]^{2+}$ than for reactions with the stronger reductant $[Cr(OH_2)_6]^{2+}$.¹ Only very few examples have been reported to date.² The widely used oxidants carboxylatopentaamminecobalt(III) complexes are predominantly reduced by V(II) via an inner-sphere mechanism with attack of the reductant at the adjacent carbonyl oxygen.³ This mechanism cannot be operative when both oxygen atoms of the carboxylic group are coordinated to two Co(III) ions as in binuclear complexes of the di- μ -hydroxo-bis[triamminecobalt(III)] type.⁴ Therefore, it seemed interesting to study the kinetics of the reductions by V(II) of the two binuclear cobalt(III)-ammine complexes with acetylenedicarboxylic acid and fumaric acid as bridging ligands (complexes I and II), since both complexes are reduced by Cr(II) via inner-sphere mechanisms with attack of the reductant at the remote carboxylic groups.^{5,6}



Experimental Section

Reagents. The binuclear complexes were prepared as described previously.^{6,7} Solutions of $[V(OH_2)_6]^{2+}$ ions in perchloric acid were prepared by electrolytic reduction of vanadium(IV) solutions under an argon atmosphere. Lithium perchlorate was obtained from Li_2CO_3 and concentrated $HClO_4$ and was purified by recrystallization.

Kinetic Measurements. The V(II) reductions of complex I at 25 and 39.6 °C were followed on a Durrum stopped-flow spectrophotometer, Model 110, at the first absorption maximum of the binuclear complexes (λ_{max} 524 nm, ϵ 110 $dm^3 mol^{-1} cm^{-1}$). All other reductions were studied by conventional spectrophotometric methods using a Unicam SP 1700 spectrophotometer at 524 nm. The reactants were mixed using standard syringe techniques under an argon or nitrogen atmosphere. All reactions were carried out under pseudo-first-order conditions with at least a tenfold excess of reductant. The reactions were followed for 5–6 half-lives. First-order rate constants were evaluated from gradients ($\times 2.303$) of plots of $\log(A_t - A_\infty)$ against time, where A_t is the absorbance at time t and A_∞ that after the reaction is complete. The plots were linear to better than 95% completion of the reaction in all cases. Activation parameters were calculated from slopes and intercepts of Figures 1 and 2 using an unweighted nonlinear least-squares program.⁸

Determination of Dissociation Constants. Both complexes I and II can protonate in aqueous acidic solution. A value of K_a of complex I has been determined previously at 25 °C and 1.0 $mol dm^{-3}$ ionic

strength ($LiClO_4$) from spectrophotometric measurements.⁶ It was found that the actual difference of spectra of the fully protonated and deprotonated species of complex II were very small. Therefore, the acid dissociation constant of II was measured potentiometrically by titrating 0.01 $mol dm^{-3}$ complex solutions with 0.1 $mol dm^{-3}$ NaOH at three different temperatures in order to obtain the thermodynamic parameters $\Delta H_0'$ and $\Delta S_0'$ for the protonation equilibrium.⁹

Results

The stoichiometry of the reductions of complex I and II by V(II) was shown to be 2:1 (2 V(II):Co^{III}) from detailed analyses of absorbance changes during the observed single-stage reduction processes as in (1). Pseudo-first-order rate



constants (excess reductant) give strictly first-order dependencies on $[V^{2+}]$ for both reactions,⁵ and the kinetic data (Table I) are consistent with the rate law (2). Absorbance

$$-d[\text{complex}]/dt = k_V[\text{complex}][V^{2+}] \quad (2)$$

changes at 524 nm were found to be in excellent agreement with calculated values for complete reductions of two Co(III) centers, respectively, and show the reductions of the second Co(III) ions of I and II to be faster than the first. Second-order rate constants, k_V ($dm^3 mol^{-1} s^{-1}$), for both reactions were found to be dependent on H^+ concentrations (Figures 1 and 2, Table I). The hydrogen ion dependence of the reduction of I ($[H^+] = 0.02$ – $0.94 mol dm^{-3}$) is expressed by a relation of form (3). Rate constants of the reduction of II

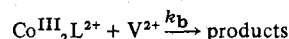
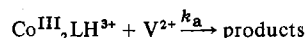
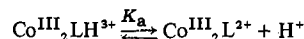
$$k_V = a + b/(c + [H^+]) \quad (3)$$

depend upon $[H^+]$ according to a simpler relation (4) ($[H^+]$

$$k_V = d + e/[H^+] \quad (4)$$

= 0.008– $0.94 mol dm^{-3}$). In a previous paper the inverse $[H^+]$ dependence has not been detected ($[H^+] = 0.7$ – $0.2 mol dm^{-3}$).⁵

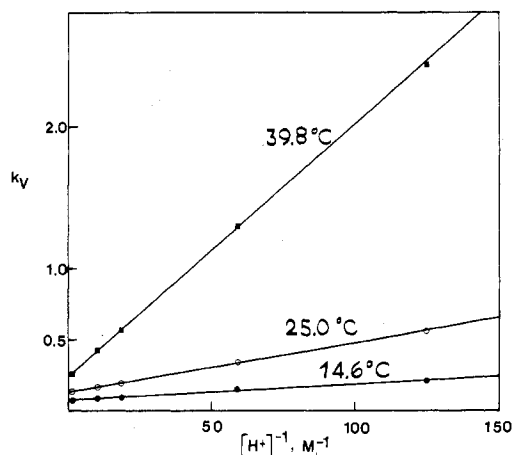
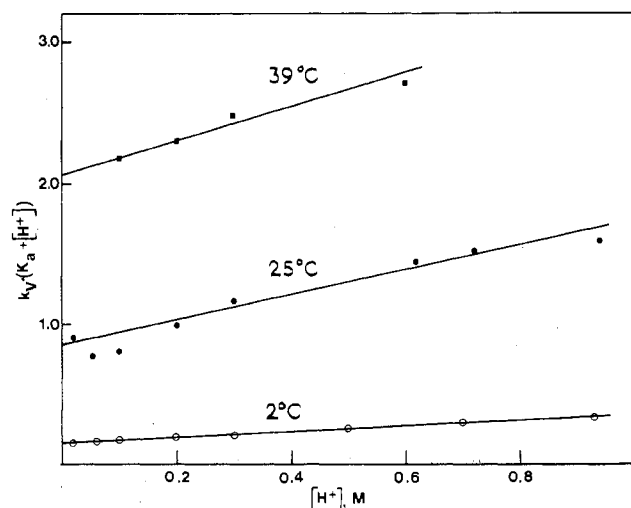
A mechanism in which the protonated ($Co^{III}_2LH^{3+}$) and deprotonated ($Co^{III}_2L^{2+}$) forms of I or II react with V(II) at different rates gives a rate law as in (5) which is of the observed form (3). (The reduction of I with $[Cr(OH_2)_6]^{2+}$ has been shown to react like this.⁶)



$$k_V = \frac{k_a[H^+] + k_bK_a}{K_a + [H^+]} = k_a + \frac{(k_b - k_a)K_a}{K_a + [H^+]} \quad (5)$$

Table I. Second-Order Rate Constants for the Reductions of Complexes I and II by Vanadium(II) at $\mu = 1.0 \text{ mol dm}^{-3}$ (LiClO_4) and $[\text{Complex}] = 0.5 \times 10^{-3} \text{ mol dm}^{-3}$

Complex I				Complex II				
$T, ^\circ\text{C}$	$[\text{H}^+], \text{mol dm}^{-3}$	$10^2 [\text{V}^{2+}], \text{mol dm}^{-3}$	$k_V, \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$	$T, ^\circ\text{C}$	$[\text{H}^+], \text{mol dm}^{-3}$	$10^2 [\text{V}^{2+}], \text{mol dm}^{-3}$	$k_V, \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$	
2.0	0.02	1.99	1.13	14.6	0.008	0.893	0.208	
	0.06	1.99	0.97		0.017	1.99	0.157	
	0.10	2.00	0.85		0.055	1.96	0.096	
	0.20	1.98	0.61		0.098	1.75	0.093	
	0.30	1.97	0.49		0.94	1.97	0.071	
	0.50	1.95	0.42		25.0	0.008	0.93	0.552
	0.70	1.99	0.37			0.017	1.99	0.343
25.0	0.93	1.93	0.32	39.8	0.050	1.97	0.189	
	0.02	2.13	7.01		0.098	1.98	0.159	
	0.06	2.13	4.53		0.94	1.98	0.126	
	0.10	2.13	3.83		0.008	0.92	2.43	
	0.20	2.13	3.20		0.017	1.79	1.31	
	0.30	0.114	2.85		0.055	1.74	0.572	
	0.30	8.67	2.88		0.098	1.96	0.427	
	0.30	9.81	2.84		0.62	1.96	0.257	
39.0	0.62	2.19	1.98	0.94	1.98	0.255		
	0.94	2.19	1.52					
	0.10	2.13	10.41					
	0.20	2.13	7.43					
	0.30	2.13	6.05					
	0.60	2.96	3.82					

**Figure 1.** Dependence of the reduction rate of μ -(fumarato-*O,O'*)-di- μ -hydroxo-bis[triamminecobalt(III)] by vanadium(II) on $[\text{H}^+]^{-1}$ ($\mu = 1.0 \text{ M}(\text{LiClO}_4)$).**Figure 2.** Dependence of $k_V(K_a + [\text{H}^+])$ on $[\text{H}^+]$ for the reduction of the μ -(carboxyacetylenecarboxylato-*O,O'*)-di- μ -hydroxo-bis[triamminecobalt(III)] by vanadium(II) with $K_a = 0.11 \text{ mol dm}^{-3}$ at all temperatures.

$a = k_a$, $b = (k_b - k_a)K_a$, and $c = K_a$. Expression 5 reduces to eq 6 if $K_a \ll [\text{H}^+]$; this is of the observed form (4) for the

$$k_V = k_a + k_b K_a / [\text{H}^+] \quad (6)$$

reduction of complex II ($d = k_a$, $e = k_b K_a$). From eq 3 and 5 it follows that this scheme is only valid for the reduction of complex I if the kinetically determined value of c (eq 3) is in agreement with the dissociation constant K_a of I (eq 5). K_a has been determined spectrophotometrically: $K_a = 0.4 \pm 0.3 \text{ mol dm}^{-3}$ at 25°C and 1.0 mol dm^{-3} ionic strength.⁶ Due to only small differences of spectra of the fully deprotonated form and the protonated form of I large error limits have been attached, and it has not been possible to obtain a reproducible temperature dependence of the protonation equilibrium.

Rearrangement of eq 5 yields eq 7 and a plot of $k_V(K_a + [\text{H}^+])$ against $[\text{H}^+]$ should give straight lines with intercepts ($=K_a k_b$) and slopes ($=k_a$).

It was found that such linear behavior is best achieved at 2, 25, and 39°C with the value $K_a = 0.11 \text{ mol dm}^{-3}$. This is illustrated in Figure 2. This kinetically determined value of K_a for complex I is in reasonable agreement with the spectrophotometrically determined dissociation constant of I. From Figure 2 values for k_a and $k_b K_a$ at three temperatures for the reduction of I are readily obtained. Activation parameters for k_a and $k_b K_a$ are listed in Table II.

$\text{p}K_a$ values of complex II have been determined potentiometrically at three different temperatures: $\text{p}K_a = 3.12, 3.02$, and 2.88 (standard deviation ± 0.01) respectively at 0, 25, and 42°C . From these values thermodynamic parameters for the dissociation equilibrium have been calculated: $\Delta H_0' = 2 \pm 1 \text{ kcal mol}^{-1}$ and $\Delta S_0' = -6 \pm 3 \text{ cal K}^{-1} \text{ mol}^{-1}$. The dissociation constant of II ($K_a = 9.5 \times 10^{-4} \text{ mol dm}^{-3}$ at 25°C) is small as compared to the experimental H^+ concentrations of the reduction of II, and eq 6 holds. It is concluded that the experimental data of the reductions of both complexes are consistent with the proposed mechanism.

From Figure 2 the intercepts ($=k_b K_a$) and from Figure 1 the slopes of the straight lines ($=k_a$) are obtained as a function of the temperature. The apparent activation parameters are therefore composite (Table II) as in (8). For a few μ -dicarboxylato-di- μ -hydroxo-bis[triamminecobalt(III)]

Table II. Summary of Kinetic Parameters of the Reductions of μ -Dicarboxylato-di- μ -hydroxo-bis[triamminecobalt(III)] Complexes by Vanadium(II) at 25 °C and $\mu = 1.0 \text{ mol dm}^{-3}$ (LiClO_4)

Complex	k_a^a , $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	ΔH_a^\ddagger , kcal mol^{-1}	ΔS_a^\ddagger , $\text{cal K}^{-1} \text{ mol}^{-1}$	Mech ^d	k_b^b , $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	ΔH^\ddagger , kcal mol^{-1}	ΔS^\ddagger , $\text{cal K}^{-1} \text{ mol}^{-1}$	Mech ^d	Ref
Malonato	0.10			o.s.	Not detected				17
Terephthalato	0.096			o.s.	Not detected				18
Maleato	0.16	5.8	-42.3	o.s.	5.0 ± 0.8^e	10.6	-29.3	i.s.(?)	5
I	0.94 ± 0.02	7.0 ± 1.5	-36 ± 5	o.s.	7.5 ± 0.8^e	11 ± 0.6	-22 ± 2	i.s.	This work
II	0.12 ± 0.01	7.5 ± 0.6	-38 ± 2	o.s.	3.6 ± 0.7^e	19.4 ± 0.4	-4 ± 2	i.s.	This work

^a Protonated forms of complexes are the reactants. ^b Unprotonated forms of complexes are the reactants. ^c Composite values; not corrected for dissociation equilibria (see eq 8). ^d o.s. = outer sphere; i.s. = inner sphere. ^e Error limits are predominantly due to large uncertainties of values of K_a .

$$\Delta H^\ddagger = \Delta H_b^\ddagger + \Delta H_0'$$

$$\Delta S^\ddagger = \Delta S_b^\ddagger + \Delta S_0' \quad (8)$$

complexes the dissociation constants have been determined at 25 °C. Only for the μ -fumarato complex II has it been possible to obtain thermodynamic parameters ($\Delta H_0'$, $\Delta S_0'$) of the dissociation equilibrium. Hence, in this particular instance true activation parameters for the k_b path can be evaluated from eq 8: $\Delta H_b^\ddagger = 17 \pm 2 \text{ kcal mol}^{-1}$ and $\Delta S_b^\ddagger = +2 \pm 5 \text{ cal K}^{-1} \text{ mol}^{-1}$. In Table II true k_b values at 25 °C but only apparent activation parameters ΔH^\ddagger and ΔS^\ddagger are summarized.

Discussion

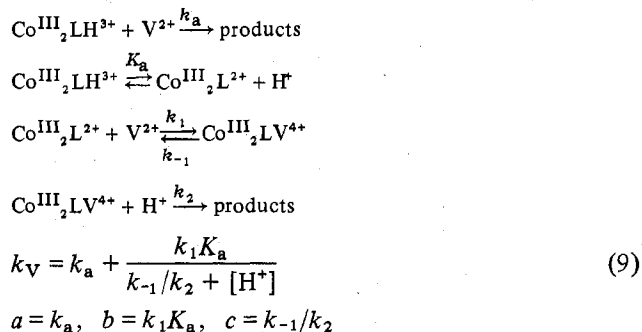
It is generally accepted that the rate-determining step of inner-sphere electron-transfer reactions of V(II) is substitution of a bridging and electron-mediating ligand into the first coordination sphere of $[\text{V}(\text{OH}_2)_6]^{2+}$.^{10,11} This assignment is based on the observation that second-order rate constants for all known inner-sphere reductions with V(II) at 25 °C have values of 1–50 $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, and what is even more indicative the activation parameters for these reactions are all in a narrow range: $\Delta H^\ddagger = 11$ –14 kcal mol^{-1} ; $\Delta S^\ddagger = 0$ to -17 $\text{cal K}^{-1} \text{ mol}^{-1}$.¹² The values reported for the simplest substitution reaction of $[\text{V}(\text{OH}_2)_6]^{2+}$, i.e., water exchange, are $\Delta H^\ddagger = 16.4 \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = +5.5 \text{ cal K}^{-1} \text{ mol}^{-1}$.¹³ The activation parameters observed for the reduction of the deprotonated form of complex II—when corrected for thermodynamic parameters of the dissociation equilibrium—are very similar. Therefore, it is concluded that the k_b path of the reduction of II occurs via an inner-sphere mechanism with precursor complex formation at the remote deprotonated carboxylic group and subsequent electron transfer through the C=C bond.

The same mechanism is assigned to the reduction of the deprotonated form of complex I, although the apparent activation parameters are not corrected for thermodynamic parameters; but a value of $k_b = 7.5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 25 °C is reasonable for substitution of a carboxylate group into $[\text{V}(\text{OH}_2)_6]^{2+}$. As has been pointed out previously an inner-sphere mechanism for the reduction of the deprotonated form of the analogous μ -maleato complex by V(II) is not readily assigned without knowledge of the thermodynamic parameters mainly because of the large negative composite activation entropy (Table II).⁵ (This would be more characteristic for an outer-sphere mechanism.) However, the dissociation constant of this complex has been determined potentiometrically at 25 °C: $K_a = 0.0089 \pm 0.002 \text{ mol dm}^{-3}$ and a value of $k_b = 5.0 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ is acceptable for a substitution-controlled process.

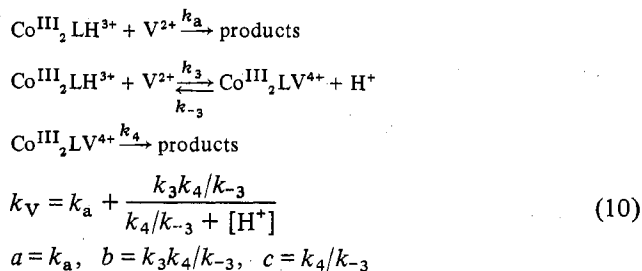
Activation parameters for the k_a path of the reductions of I and II—the protonated forms are reduced—are significantly different from those observed for the k_b path (Table II). They are certainly not in agreement with substitution-controlled inner-sphere processes. They are very similar to values observed for the reduction of mononuclear Co(III) complexes by V(II) which are known to occur via outer-sphere mechanisms.¹⁴ Therefore, it is concluded that the protonated forms

of complexes I and II react with V(II) via outer-sphere mechanisms.

Although the proposed mechanisms for the reductions of complexes I and II by V(II) are consistent with the experimental data of the present investigation, it is noted that this mechanism has been shown not to be operative when N-coordinated (nicotinic acid)- and (isonicotinic acid)pentamminecobalt(III) complexes are reduced by V(II). Norris and Nordmeyer have presented two alternate mechanisms both of which lead to the formal rate equation (3).² Their kinetic data are only consistent with mechanism II. The following schemes are adapted for the reduction of the binuclear complexes I and II: mechanism I



and mechanism II



The simplified rate equation (eq 4) is observed, if c (eq 3) is small compared to the experimental hydrogen ion concentration: $c < 0.008 \text{ mol dm}^{-3}$.

For complex I we obtain $k_1 = b/K_a = 1.8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 25 °C and for complex II $k_1 = 3.5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Both values are acceptable (although at a lower limit) for the substitution of a $-\text{COO}^-$ group into V^{2+} . Therefore, mechanism I is also consistent with our kinetic data—contrary to Nordmeyer's results where k_1 exceeds the specific rate of substitution on V^{2+} .

Mechanism II on the other hand cannot be operative for the V^{2+} reduction of complex I because under our experimental conditions ($[\text{H}^+] = 0.02$ – 0.94 mol dm^{-3}) appreciable concentrations of the unprotonated complex I are present. For complex II only a lower limit for $k_3 = b/c > 3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ can be estimated.

In summary, no simple common reaction scheme for the V^{2+} reduction of mononuclear and binuclear carboxylatocobalt-

(III)-ammine complexes can presently be offered. Despite this disturbing aspect it is of interest to note that an outer-sphere path is observed for the protonated forms of all complexes. In addition, inner-sphere type mechanisms appear to occur also in all cases with attack of the reductant at the remote carboxylic group (protonated or unprotonated) and intramolecular transfer of an electron within cobalt(III)-vanadium(II) intermediates (in a protonated or deprotonated form).

Electron transfer through extended organic bridging ligands with $[\text{Cr}(\text{OH}_2)_6]^{2+}$ as reductant is observed (a) if the uncomplexed organic ligand is reducible by Cr(II) and (b) if conjugation from the electron donor to the acceptor is given.¹⁵ We propose that the same conditions also apply for the reductions of binuclear cobalt(III)-ammine complexes with V(II) as reductant. Fumaric acid and maleic acid¹⁶ as well as acetylenedicarboxylic acid are reducible by V(II) and have good conjugation. Other data from Table II are in line with this interpretation. For the reduction of the μ -malonato complex by V(II) only an outer-sphere mechanism is detected¹⁷ due to the lack of conjugation whereas the μ -terephthalato complex is reduced via an outer-sphere mechanism because of its irreducibility.¹⁸ There appears to be only one serious exception to this scheme. The nonreducible pyridine-3-carboxylic acid is reported to function as an electron-mediating ligand when the N-coordinated (pyridine-3-carboxylato)-pentaamminecobalt(III) complex is reduced by V(II).² The pyridine-4-carboxylato analogue on the other hand fits.

For reasons not yet understood the protonated forms of I and II are reduced by V(II) via outer-sphere mechanisms—when $[\text{Cr}(\text{OH}_2)_6]^{2+}$ is the reductant inner-sphere paths are observed.^{5,6} Compared with Cr(II) $[\text{V}(\text{H}_2\text{O})_6]^{2+}$ is a much weaker reductant. This may account for a pronounced selectivity of V(II) regarding its capability to

function as an inner-sphere reagent with attack at a remote polar group of the organic bridging ligand. Protonation of the remote carboxylic group may affect the lowest unoccupied antibonding orbital of I and II to such a degree that an inner-sphere path becomes energetically unfavorable. This interpretation is somewhat vitiated by the observation that the protonated form of I is reduced more rapidly than the unprotonated form if $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ is the reductant.⁶

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Registry No. I, 61168-66-9; II, 58769-41-8; $\text{V}(\text{OH}_2)_6^{2+}$, 15696-18-1; H^+ , 12408-02-5.

References and Notes

- (1) J. C. Chen and E. S. Gould, *J. Am. Chem. Soc.*, **95**, 5539 (1973).
- (2) C. Norris and F. R. Nordmeyer, *Inorg. Chem.*, **10**, 1235 (1971).
- (3) M. B. Barrett, J. H. Swinehart, and H. Taube, *Inorg. Chem.*, **10**, 1985 (1971).
- (4) K. Wieghardt and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 651 (1974).
- (5) M. R. Hyde, K. L. Scott, K. Wieghardt, and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 153 (1976).
- (6) M. Hery and K. Wieghardt, *J. Chem. Soc., Dalton Trans.*, 1536 (1976).
- (7) K. Wieghardt, *J. Chem. Soc., Dalton Trans.*, 2548 (1973).
- (8) R. H. Moore and R. K. Zeigler, Los Alamos Report LA 2367 (1959) and Addenda.
- (9) A. Albert and E. Serjeant, "The Determination of Ionization Constants", Chapman and Hall, London, 1971.
- (10) N. Sutin, *Acc. Chem. Res.*, **1**, 225 (1968).
- (11) R. G. Linck, *MTP Int. Rev. Sci.: Inorg. Chem., Ser. One*, **9**, 303 (1972).
- (12) A. McAuley, *Inorg. React. Mech.*, **2**, 15 (1972).
- (13) M. V. Olson, Y. Kanazawa, and H. Taube, *J. Chem. Phys.*, **51**, 289 (1969).
- (14) D. P. Rillema and J. F. Endicott, *Inorg. Chem.*, **11**, 2361 (1972).
- (15) H. Taube and E. S. Gould, *Acc. Chem. Res.*, **2**, 321 (1969).
- (16) A. Malliaris and D. Katakis, *J. Am. Chem. Soc.*, **87**, 3077 (1965).
- (17) B. Kipling, K. Wieghardt, M. Hery, and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 2176 (1976).
- (18) M. Hery and K. Wieghardt, *Inorg. Chem.*, **15**, 2315 (1976).

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Kinetic and Electron Spin Resonance Spectroscopic Evidence for a Chemical Mechanism in the Chromium(II) Reduction of Two (Pyrazinecarboxylato)amminecobalt(III) Complexes

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The reductions of the mononuclear complex (pyrazinecarboxylato)pentaamminecobalt(III) (A) and the binuclear complex μ -pyrazinecarboxylato(*O,O'*)-di- μ -hydroxo-bis[triamminecobalt(III)] (B) by $\text{Cr}(\text{H}_2\text{O})_6^{2+}$ have been studied. Kinetic and ESR spectroscopic measurements indicate the formation of transient radical species. Direct evidence for the occurrence of a chemical mechanism has been obtained for the Cr^{2+} reduction of complex A.

Inner-sphere electron transfer between two metal ions in solution is effected by means of a bridging ligand which is coordinated to both metal centers in the precursor complex. The bridging ligand can help to increase the probability of electron transfer by tunneling ("resonance transfer"), or the ligand can accept an electron, generating a radical intermediate, and in a subsequent step the electron is passed onto the oxidant center ("chemical, radical or two-step mechanism").¹⁻³ Assignment of the latter mechanism for the Cr^{2+} reduction of Co(III) and Cr(III) complexes via the same organic bridging ligand is based mainly on indirect criteria such as comparison of rates.⁴

In 1972 Gould reported the spectrophotometric detection of a reactive, strongly absorbing intermediate in the Cr^{2+} reduction of the (pyrazinecarboxylato)pentaamminecobalt(III) complex (A).⁵ From the kinetic behavior of the formation and subsequent decay of this transient species he assigned structure II (see Scheme I) in which the electron is located on the organic ligand.

We have studied the kinetics of the Cr^{2+} reduction of the binuclear μ -pyrazinecarboxylato-di- μ -hydroxo-bis[triamminecobalt(III)] complex (B). Reduction of the first Co(III) center should occur with remote attack of the reductant at either of the two heterocyclic nitrogen atoms, but