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Selectivity of Outer-Sphere Electron-Transfer Reactions. 3

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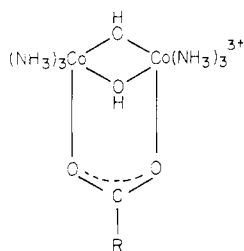
The study of the kinetics of the reductions of a series of binuclear (μ -carboxylato)bis(μ -hydroxo)bis[triamminecobalt(III)] complexes has been extended to more powerful reducing agents. It was found that for very exothermic reactions the selectivity becomes independent of the redox potential of the reductant. The results are analyzed in the frame of the full Marcus formalism.

Introduction

Recently the kinetics of the outer-sphere reductions of a series of binuclear (μ -carboxylato)bis(μ -hydroxo)bis[triamminecobalt(III)] complexes by reductants such as $\text{Cr}(\text{OH})_2^{2+}$, $\text{V}(\text{OH})_2^{2+}$, $\text{Ru}(\text{NH}_3)_6^{2+}$, $\text{Ti}(\text{dipic})_2^-$, $\text{Fe}(\text{dipic})_2^{2-}$ (dipic = pyridine-2,6-dicarboxylate) have been reported.²

It was shown that the logarithms of the second-order rate constants, k_{red} , vary linearly with Taft's inductive parameter, σ_1 , for substituents, R, of the coordinated carboxylate groups. Since $k_{\text{red}} = k_{\text{et}}K_0$ (K_0 is the ion-pair association constant of oxidant and reductant and k_{et} is the intermolecular electron-transfer rate constant), the observed inductive effect reflects the increasing oxidizing ability of the Co(III) centers within the redox-active ion pairs, and $k_{\text{et}}^{\text{CF}_3} > k_{\text{et}}^{\text{CHF}_2} > k_{\text{et}}^{\text{CH}_2\text{F}} > k_{\text{et}}^{\text{CH}_3}$.

For a given reductant values of K_0 for the above series of binuclear oxidants do not vary due to the structural similarity of complexes I-IV. It was found that the slopes of plots of



- I, R = CF_3
 II, R = CHF_2
 III, R = CH_2F
 IV, R = CH_3

$\log k_{\text{red}}$ vs. σ_1 are linearly correlated with the half-wave potentials of the reductants: the stronger the reductant (i.e., more negative reduction potential, E°_{B}), the smaller is the observed selectivity (eq 1). The selectivity is defined as the difference

$$\log k_{\text{red}}^{\text{CF}_3} - \log k_{\text{red}}^{\text{CH}_3} = 0.95E^\circ_{\text{B}} + 1.0 \quad (1)$$

of the logarithms of the second-order rate constants for the reductions of two oxidizing complexes by a given reductant; i.e., E°_{B} of the reductants of the earlier study² varied between +0.28 and -0.40 V. It seemed of interest to check whether the linear relationships of the rate constants of reaction with σ_1 and of the selectivity with E°_{B} hold also for reactions with a larger free energy gain (i.e., reactions with stronger reductants). As most of the powerful outer-sphere reductants are short-lived in aqueous solution, we have chosen the pulse-radiolytic technique for this study.

The analysis of the results suggests that the dependence of the selectivity on E°_{B} stems from the expression

$$\Delta G^\ddagger = \frac{\lambda}{4} \left(1 + \frac{\Delta G^\circ_{\text{AB}}}{\lambda} \right)^2 \quad (2)$$

where λ is the energy of reorganization and $\Delta G^\circ_{\text{AB}}$ is the free energy change of the reaction. The selectivity becomes independent of E°_{B} for very exothermic reactions ($-\Delta G^\circ_{\text{AB}} \geq \lambda$), when eq 2 loses its validity.³

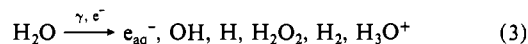
Experimental Section

Materials. The binuclear complexes of cobalt(III) used were identical with those described earlier.² All solutions were prepared using triple-distilled water, or water from a Millipore Milli Q 2 setup. All other chemicals were of AR grade and were used without further treatment.

Irradiations. The pulse-radiolytic experiments were carried out with 0.5-1.5- μs , 5-MeV, 200-mA pulses from the electron linear accelerator at the Hebrew University of Jerusalem. The dose per pulse was 150-3000 rd. The experimental setup and the methods used for evaluating the results have been described elsewhere in detail.⁴

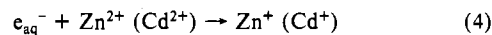
Kinetics. Solutions were saturated with N_2O or Ar before irradiations. The kinetics of formation and of bleaching of absorbance were followed. Pseudo-first- or second-order rates were calculated when the kinetic plot indicated first- or second-order behavior for at least 3 half-lives. All experiments were carried out at room temperature, $22 \pm 2^\circ\text{C}$.

Production of Reducing Reagents. The radiolysis of water by ionizing radiation can be described by the equation⁵



The yields of the products are $G(e_{\text{aq}}^-) = 2.65$, $G(\text{OH}) = 2.65$, $G(\text{H}) = 0.60$, $G(\text{H}_2) = 0.45$, and $G(\text{H}_2\text{O}_2) = 0.75$ (where the G value is the number of product molecules formed by the absorption of 100 eV in the solution). Somewhat higher yields are expected in concentrated solutions. The products are homogeneously distributed within less than 10^{-7} s after the absorption of the radiation.

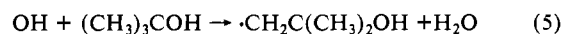
Reactions with Zn^{2+} and Cd^{2+} . Argon-saturated solutions containing 0.1 M MSO_4 ($\text{M} = \text{Zn}, \text{Cd}$) and 0.1 M $(\text{CH}_3)_3\text{COH}$ were irradiated. Under these conditions all e_{aq}^- react via eq 4, where k are the ap-



$$k_{e_{\text{aq}}^- + \text{Zn}^{2+}} = 2.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-16}$$

$$k_{e_{\text{aq}}^- + \text{Zn}^{2+}} = 5.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-16}$$

propriate rate constants, and all OH radicals react via eq 5. Both



$$k = 5.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-17}$$

Zn^+ and Cd^+ decompose via a diffusion-controlled second-order re-

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Table I. Summary of Kinetic Data $k_{\text{red}} = k_{\text{et}}K_{\text{O}}$ ($\text{M}^{-1} \text{s}^{-1}$) for the Reductions of (μ -Carboxylato)dicobalt(III) Cations by Various Reductants

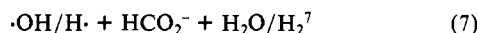
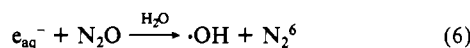
reductant/complex	CH ₃	CH ₂ F	CHF ₂	CF ₃	E°_{12} , V	ref
Fe(dipic) ₂ ²⁻ ^a	1.43×10^{-2}	5.1×10^{-2}	11.9×10^{-2}	28.6×10^{-2}	+0.28	2
Ru(NH ₃) ₆ ²⁺	0.035	0.12	0.21	0.36	+0.100 ²²	2
V(OH ₂) ₆ ²⁺	0.062	0.13	0.21	0.38	-0.230	2
Cr(OH ₂) ₆ ²⁺	1.46×10^{-3}	2.79×10^{-3}	3.97×10^{-3}	6.3×10^{-3}	-0.45	2
Eu(OH ₂) ₆ ²⁺	1.35×10^{-2}			7.4×10^{-2}	-0.38	2
NiL ⁺ ^b	8.8×10^4	1.4×10^5	1.8×10^5	3.0×10^5	-0.74 ¹¹	this work
Zn ⁺ (aq)	5.5×10^8	7.6×10^8	1.0×10^9	1.15×10^9	-2.0 ¹³	this work
Cd ⁺ (aq)	2.2×10^8	3.0×10^8	3.6×10^8	4.1×10^8	-1.8 ¹³	this work
·CO ₂ ⁻	5.8×10^7	1.1×10^8	2.4×10^8	3.5×10^8	-1.3 ¹⁴	this work
pyridine-4-carboxamide radical	9.1×10^6	1.9×10^7	3.5×10^7	5.6×10^7	-0.80 ¹²	this work

^a dipic = pyridine-2,6-dicarboxylate. ^b L = *meso*-1,4,5,7,7,8,11,12,14,14-decamethyl-1,4,8,11-tetraazacyclotetradecane.

action⁸ and probably also via reaction with ·CH₂C(CH₃)₂OH. (The latter reaction was reported for Cd⁺^{9,10a} but occurs also for Zn⁺.) However, when high enough concentrations of other oxidants such as Co(III) complexes are present, the reaction of M⁺ with these oxidants can be followed spectrophotometrically since both Zn⁺ and Cd⁺ have strong absorption bands in the near-UV region.⁸

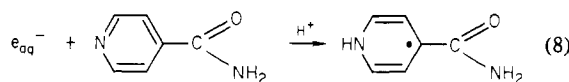
Reactions with (*meso*-1,4,5,7,7,8,11,12,14,14-Decamethyl-1,4,8,11-tetraazacyclotetradecane)nickel(I), NiL⁺. Although NiL⁺ is stable in aqueous solution and can be prepared by preparative electrochemical reduction¹¹ of NiL²⁺, it was easier for us to use the pulse-radiolytic technique also for the study of reductions by NiL⁺. ($k_{\text{e}_{\text{aq}}^- + \text{NiL}^{2+}} = 8 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$; and no reaction of ·CH₂C(CH₃)₂OH with NiL⁺ is observed.¹¹) NiL⁺ has an absorption maximum at 335 nm, and its reactions were followed by observing the decrease of the absorption due to it.

Reactions with ·CO₂⁻. N₂O-saturated solutions containing 0.1 M NaHCO₂ were irradiated. Under these conditions the following reactions have to be considered:



·CO₂⁻ absorbs light only in the far-UV region, and therefore, we followed its reactions by monitoring the decrease in absorbance due to the Co(III) complexes.

Reactions with the Pyridine-4-carboxamide Radical. Argon-saturated solutions at pH ~4 containing 0.5 M (CH₃)₃COH and 2×10^{-3} – 1×10^{-2} M pyridine-4-carboxamide were irradiated. Under these conditions the hydrated electrons react via eq 8. The radical produced



exhibits a strong absorption maximum at 395 nm.¹² It does not react with the ·CH₂C(CH₃)₂OH radicals formed in reaction 5. Its pK_a is 1.9.^{10b}

Results and Discussion

In Table I the kinetic data are summarized for the reductions of the series of structurally very similar binuclear (μ -carboxylato)dicobalt(III) complexes by various reductants. We measured also the rates of reactions of these complexes with Tl₂⁺ and the pyridine-3-carboxamide radical; they ap-

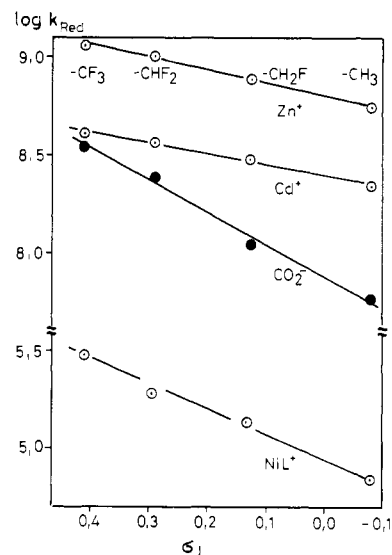


Figure 1. Correlation of the logarithms of the second-order rate constants of the reductions of binuclear cobalt(III) complexes I, II, III, and IV by the reductants Zn⁺(aq), Cd⁺(aq), ·CO₂⁻, and NiL⁺, respectively, as Taft's inductive parameter, σ_I .

proach the diffusion-controlled limit, are therefore of little mechanistic interest, and were not included in the table. The corresponding reactions with the pyrazine and nitrobenzoato radicals were found to be too slow to be measured by the pulse-radiolytic technique. Figure 1 demonstrates that again linear correlations are observed between $\log k_{\text{red}}$ and Taft's inductive parameters, σ_I . The order of reactivity is the same for all reductants used ($k_{\text{red}}^{\text{CF}_3} > k_{\text{red}}^{\text{CHF}_2} > k_{\text{red}}^{\text{CH}_2\text{F}} > k_{\text{red}}^{\text{CH}_3}$), reflecting the decreasing driving force, $\Delta G^{\circ}_{\text{AB}}$.

The rate of reaction (for $|\Delta G^{\circ}_{\text{AB}}| < \lambda$) can be expressed according to the Marcus theory¹⁵ as

$$k_{\text{A}_i\text{B}} = \kappa_{\text{A}_i\text{B}} e^{-(\Delta G^{\circ}_{\text{A}_i\text{B}} + \lambda)^2 / 4\lambda RT} \quad (9)$$

where A_i represents one of the binuclear Co(III) complexes and B the reducing agent. In writing λ without a subscript, we assume that within the series of oxidants, A_i, λ does not vary for a given reductant. This assumption is reasonable as the Co(III) complexes studied are structurally very similar and inner-sphere as well as outer-sphere reorganization energies should also be very similar. $\kappa_{\text{A}_i\text{B}}$ is the preexponential factor and

$$\Delta G^{\circ}_{\text{A}_i\text{B}} = G^{\circ}_{\text{A}_i^-} + G^{\circ}_{\text{B}^+} - G^{\circ}_{\text{A}_i} - G^{\circ}_{\text{B}} = \Delta G^{\circ}_{\text{A}_i} - \Delta G^{\circ}_{\text{B}} \quad (10)$$

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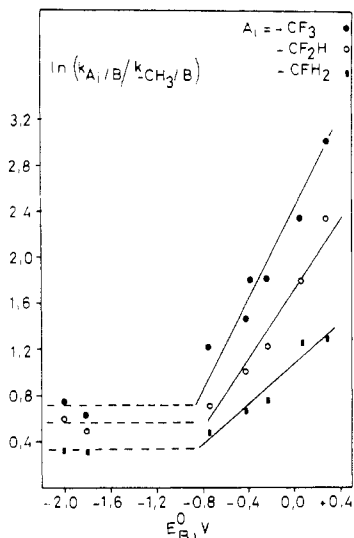


Figure 2. Plot of the selectivities, $\ln(k_{A_i/B}/k_{CH_3/B})$, vs. redox potential of the reductants, E°_B .

where all the ΔG 's are expressed for reduction reactions. Therefore

$$\ln(k_{A_i/B}/k_{A_j/B}) = \ln(k_{A_i/B}/k_{A_j/B}) + \frac{1}{4\lambda RT} [(\Delta G^{\circ}_{A_j/B} + \lambda)^2 - (\Delta G_{A_i/B} + \lambda)^2] \quad (11)$$

Equation 11 can be reformulated as

$$\ln(k_{A_i/B}/k_{A_j/B}) = \ln(k_{A_i/B}/k_{A_j/B}) + \frac{1}{4\lambda RT} [(\Delta G^{\circ}_{A_j})^2 - (\Delta G^{\circ}_{A_i})^2 + 2\lambda(\Delta G^{\circ}_{A_j} - \Delta G^{\circ}_{A_i})] - \left(\frac{\Delta G^{\circ}_{A_j} - \Delta G^{\circ}_{A_i}}{2\lambda RT} \right) (\Delta G^{\circ}_B) \quad (12)$$

One thus expects that a plot of $\ln(k_{A_i/B}/k_{A_j/B})$ vs. ΔG°_B will result in a straight line with a slope of

$$-(\Delta G^{\circ}_{A_j} - \Delta G^{\circ}_{A_i})/2\lambda RT$$

For very exothermic reactions $k_{A_i/B}$ becomes independent of $\Delta G^{\circ}_{A_i}$,³ and therefore $k_{A_i/B} = k'_{A_i/B}$ and $k_{A_j/B} = k_{A_j/B}$. For such exothermic reactions $\ln(k_{A_i/B}/k_{A_j/B}) = \ln(k'_{A_i/B}/k_{A_j/B})$, i.e., becomes independent of ΔG°_B .

The intersection between the two types of dependencies on ΔG°_B defined by extrapolation of the appropriate two equations is given by eq 13 and 14. Of course, in practice the

$$\ln(k'_{A_i/B}/k'_{A_j/B}) = \ln(k_{A_i/B}/k_{A_j/B}) + \frac{1}{4\lambda RT} [(\Delta G^{\circ}_{A_j})^2 - (\Delta G^{\circ}_{A_i})^2 + 2\lambda(\Delta G^{\circ}_{A_j} - \Delta G^{\circ}_{A_i})] - \frac{\Delta G^{\circ}_{A_j} - \Delta G^{\circ}_{A_i}}{2\lambda RT} \Delta G^{\circ}_B \quad (13)$$

$$\Delta G^{\circ}_B(\text{intersection}) = \lambda + \frac{\Delta G^{\circ}_{A_j} + \Delta G^{\circ}_{A_i}}{2} - \frac{2\lambda RT}{\Delta G^{\circ}_{A_j} - \Delta G^{\circ}_{A_i}} \ln \left(\frac{k'_{A_i/B} k_{A_j/B}}{k'_{A_j/B} k_{A_i/B}} \right) \quad (14)$$

transition between the two behaviors is gradual.

If one assumes that $(k'_{A_i/B} k_{A_j/B}/k'_{A_j/B} k_{A_i/B}) \cong 1$ i.e., that the Franck-Condon parameters for the reduction of the two Co(III) complexes are nearly equal, then eq 15 holds. Numerical

$$\Delta G^{\circ}_B(\text{intersection}) = \lambda + \frac{\Delta G^{\circ}_{A_j} + \Delta G^{\circ}_{A_i}}{2} \quad (15)$$

values of $\ln(k_{A_i/B}/k_{A_j/B})$ for three pairs of oxidants are plotted in Figure 2 vs. the redox potential of the reducing agent E°_B , which equals $-\Delta G^{\circ}_B + \text{const}$. Indeed, it is found that for each couple of cobalt(III) complexes studied $\ln k_{A_i/B}$ changes linearly with E°_B over a wide range and that for highly exothermic reactions no dependence of the selectivity on E°_B is observed.

It should be noted that the linear relationship observed indicates that λ is nearly independent of the nature of the reductant B, a result which is somewhat surprising in view of the diversity of reductants used. This observation might be rationalized if the main contribution to λ in these reactions stems from the rearrangement around the cobalt centers.

It is interesting that the results for the reductions with the nonmetal reductants $\cdot\text{CO}_2^-$ and the pyridine-4-carboxamide radical do not fall on the lines in Figure 2.¹⁶

From the slopes of the straight lines in Figure 2 we calculate $\Delta G^{\circ}_{A_j} - \Delta G^{\circ}_{A_i} = 0.1\lambda, 0.08\lambda,$ and 0.05λ for $A_i = R = \text{CH}_3$ (complex IV) and $A_j = R = \text{CF}_3, \text{CF}_2\text{H},$ and CFH_2 (complexes I-III), respectively. The intersection between the region where $\ln(k_{A_i/B}/k_{A_j/B})$ depends on ΔG°_B and that where it is independent occurs at $E^{\circ}_B \approx -0.8\text{V}$. The redox potentials of the cobalt(III) complexes are ca. $+0.6\text{V}$. Thus, $\lambda \approx 1.4\text{V}$ and $\Delta G^{\circ}_{A_j} - \Delta G^{\circ}_{A_i} \approx 0.14, 0.11,$ and 0.07V , respectively. These estimated small differences in the redox potentials of the cobalt(III) complexes used in this study are considered to be reasonable.

A similar linear dependence between the selectivity in the reductions of $[\text{Co}(\text{NH}_3)_5\text{OH}_2]^{3+}$ and $[\text{Co}(\text{NH}_3)_6]^{3+}$ by different reductants and the latter's redox potentials has also been reported.¹⁸ As the redox potentials for these Co(III) complexes are 0.35V for $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ and 0.11V for $[\text{Co}(\text{NH}_3)_6]^{3+}$, we calculate $\lambda \approx 1.7\text{V}$ from the slope.^{19,20}

In conclusion we present experimental results indicating that the selectivity of the rates of the outer-sphere redox processes studied ceases to depend on the free energy gain for high exothermicities (as compared to reorganization energy). We show that we can rationalize the results over the whole range of free energy gain by putting to careful use the Marcus theory for outer-sphere electron-transfer reactions. Specifically the analysis shows that some results which seem to deviate from the Marcus relations in their linear approximation fit the theory when the quadratic terms are included.

Registry No. I, 46753-32-6; II, 46470-29-5; III, 46362-08-7; IV, 46240-70-4; NiL⁺, 84026-55-1; Zn, 7440-66-6; Cd, 7440-43-9; $\cdot\text{CO}_2^-$, 34496-91-8; pyridine-4-carboxamide radical, 57625-96-4.

- (16) This could be due to several reasons: (1) The reductions by organic free radicals might not follow the outer-sphere mechanism, as has been concluded for reductions with some aliphatic free radicals.¹⁷ (2) λ might have a considerably lower value as the results seem to indicate that $\ln(k_{A_i/B}/k_{A_j/B})$ becomes independent of E°_B for much weaker reducing agents. However, this is an unreasonable assumption if the major contribution to λ stems from rearrangements of the cobalt complexes. (3) λ might have a considerably higher value, which will result in a smaller slope of the linear relation.
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- (19) The rate of reduction of $\text{Co}(\text{NH}_3)_6^{3+}$ and of $\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}$ by Cd^+ has been reported to be significantly below the diffusion-controlled limit.⁸ Since $E^{\circ}_B(\text{Cd}^+/\text{Cd}^{2+}) \approx -1.8\text{V}$ ¹³ and $\log(k_{\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}}/k_{\text{Co}(\text{NH}_3)_6^{3+}}) = 0.56$,⁸ the point for the reductions of these two oxidants by Sm^{2+} ($E^{\circ}_B = -1.5\text{V}$) on the plot in ref 18 seems to indicate an experimental error or a different mechanism.
- (20) Recently Frese²¹ estimated λ for a series of redox reagents. His estimates are considerably larger than those reported in the present study. However, he used the static dielectric constant for calculating the electrostatic work term in ΔG^* . Therefore, his estimates of λ tend to be too large.
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