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Intramolecular Electron Transfer at Metal Surfaces. 3. Influence of Bond Conjugation on Reduction Kinetics of Cobalt(III) Anchored to Electrodes via Thiophenecarboxylate Ligands

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Abstract: Unimolecular rate constants, k_{et}, are reported for the one-electron electroreduction of pentaamminecobalt(III) anchored to mercury, gold, or copper electrodes via various thiophenecarboxylate ligands where the thiophene sulfur acts as the surface binding group and the carboxylate is coordinated to the cobalt reactants. At mercury, the rate parameters were found to be sensitive to the bridging ligand structure, substantially (ca. 10–20-fold) smaller values of k_{et} being found for ligands containing one or more methylene groups between the thiophene sulfur and carboxylate oxygen than those featuring uninterrupted bond conjugation between the metal surface donor and Co(III) acceptor sites. Various contributions to these reactivity differences are assessed on the basis of the measured variations in the stability constants of the adsorbed precursor state, the rate constants for the homogeneous reduction of these complexes by hexaammineruthenium(II), the unimolecular frequency factors obtained from the electrochemical activation parameters, and by comparison with electrochemical outer-sphere rate data. Taken together, these results provide strong evidence that the smaller values of k_{et} seen with the nonconjugated bridging ligands are due predominantly to smaller values of the electronic transmission coefficient than are achieved with the conjugated ligands. Comparison is made with analogous results for intramolecular electron transfer via extended organic ligands in homogeneous solution.

Introduction

The mediation of electron-transfer reactions between transition-metal redox centers by organic bridging ligands has received a great deal of attention over the last 20 years or so.[1] An increasingly detailed picture has emerged of the various structural and electronic factors that underlie the substantial variations in reactivity that result from altering the nature of the bridging ligand as well as the metal ions. Valuable insights into the reaction energetics have been obtained with the advent of rate measurements for intramolecular electron transfer within binuclear complexes.[1d-h] Studies of intramolecular reactivities have the crucial virtue of providing direct information on the energetics of the elementary electron-transfer step for geometrically well-defined systems. They also avoid the uncertainties associated with precursor complex formation that are inherent in the treatment of bimolecular electron-transfer processes.

A key question that has been addressed in these studies is the degree to which efficient electronic coupling, and hence the electron tunneling probability κ_{el}, is influenced by the donor–acceptor separation between them and the structure of the intervening organic bridge.[1f,g] The information gathered so far indicates that adiabatic pathways ($\kappa_{el} \sim 1$) require the presence of a fully conjugated bridge, markedly nonadiabatic pathways ($\kappa_{el} \ll 1$) being encountered upon the introduction of saturated linkages.[1f,g]

Such electronic factors might also be anticipated to have a major influence upon the kinetics of electron-transfer processes at metal–electrolyte interfaces. Although most of the concepts and theoretical relations which have been developed directly for solution redox processes can be transposed directly to the heterogeneous case, one difference is that metal surfaces provide an effective continuum of electronic states. This has led to the assertion that electrochemical reactions should generally be adiabatic.[2] Unfortunately, despite the practical and fundamental importance of electrochemical processes, the pertinent experimental data with which to examine such fundamental questions have largely been lacking.

We have recently been examining simple one-electron electrochemical reactions involving transition-metal reactants that bind to metal surfaces via one or more bridging ligands.[3] Systems were selected that are sufficiently strongly adsorbed to enable unimolecular rate constants, k_{et}, to be obtained for the elementary electron-transfer step involving the surface-attached reactant. Such reactions can be perceived as involving "surface intramolecular" electron transfer since they are entirely analogous to redox processes involving binuclear metal complexes, the metal surface being substituted for one of the redox centers. Despite the recent widespread interest in the electrochemistry of surface-attached molecules, virtually no kinetics data have been gathered previously for such systems.

In parts I and II of this series,[3a,b] we examined in detail the electroreduction kinetics of various Co(III) and Cr(III) complexes adsorbed via halide and pseudohalide bridging ligands at platinum, gold, mercury, and silver surfaces. Comparisons were made between values of k_{et} determined for a given bridging ligand at different metal surfaces and with estimates of k_{et} for the corresponding outer-sphere processes.[3] These results demonstrate that the alteration in the electron-transfer barrier brought about by surface attachment is sensitive both to the chemical nature of the bridge and the metal surface.

Similar strategies can usefully by followed for examining the factors influencing the mediation of heterogeneous electron-transfer processes by extended organic ligands. Thus it is desirable to select organic ligands containing a remote "lead-in" group capable of binding strongly to metal surfaces in addition to having a convenient coordination site for a metal redox center. We have recently examined pyrazine, 4,4′-bipyridine, and related ligands as bridging groups for pentaamminecobalt(III) reduction at mercury, platinum, and gold surfaces.[4] While several of these ligands are detectably adsorbed and yield facile inner-sphere pathways, nitrogen typically appears to be only a mediocre surface lead-in group so that direct measurements of k_{et} are largely

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(1) For reviews, see: (a) Taube, H.; Gould, E. S. *Acc. Chem. Res.* **1969**, *2*, 321. (b) Taube, H. *Pure Appl. Chem.* **1970**, *24*, 289. (c) Taube, H. *Ber. Bunsenges. Phys. Chem.* **1972**, *76*, 964. (d) Haim, A. *Acc. Chem. Res.* **1975**, *8*, 264. (e) Linck, R. G. *Surv. Prog. Chem.* **1976**, *7*, 89. (f) Taube, H. *Adv. Chem. Ser.* **1977**, No. *162*, 127. (g) Taube, H. In "Tunneling in Biological Systems"; Chance, B., DeVault, D. C., Frauenfelder, H., Marcus, R. A., Schrieffer, J. R., Sutin, N., Eds.; Academic Press: New York, 1979, p 173. (h) Haim, A. *Prog. Inorg. Chem.* **1983**, *30*, 273.

(2) (a) Hale, J. M. *J. Electroanal. Chem.* **1968**, *19*, 315. (b) Hale, J. M. "Reactions of Molecules at Electrodes"; Hush, N. S. Ed.; Interscience: New York, 1971; Chapter 4. (c) Doganadze, R. R.; Kuznetsov, A. M.; Vorotyntsev, M. A.; *J. Electroanal. Chem.* **1970**, *25*, App 17.

(3) (a) Barr, S. W.; Weaver, M. J. *Inorg. Chem.*, in press. (b) Guyer, K. L.; Weaver, M. J. *Ibid.*, in press.

(4) Srinivasan, V.; Barr, S. W.; Weaver, M. J. *Inorg. Chem.* **1982**, *21*, 3154.

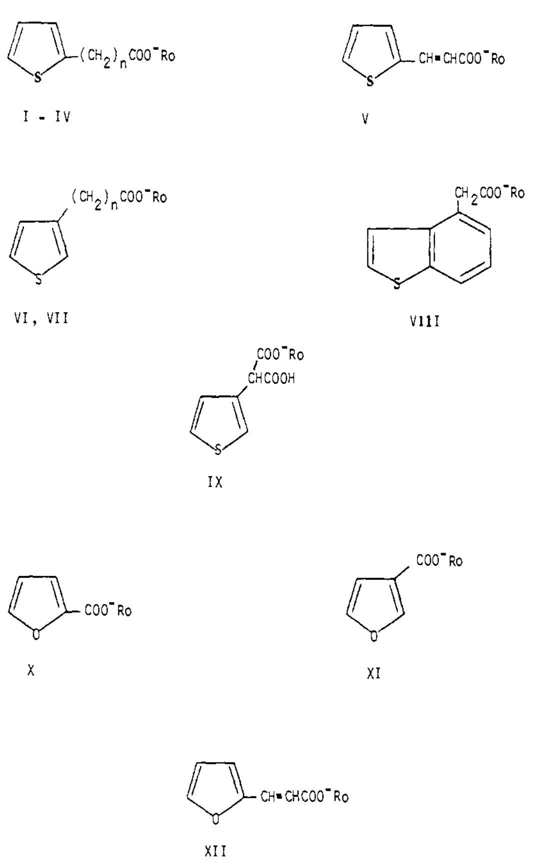

Figure 1. Structures of thiophene- and furan-carboxylatopentaamminecobalt(III) complexes studied in the present work. Key (Ro = $Co^{III}(NH_3)_5$): I, *n* = 0; II, *n* = 1; III, *n* = 2; IV, *n* = 3; VI, *n* = 0, VII, *n* = 1.

precluded.[4] Notably stronger surface coordination is provided by sulfur atoms having an available lone pair, reflecting the "soft acceptor" properties of metal surfaces.[5]

Such considerations led us to select for further study the reduction of a series of pentaamminecobalt(III) complexes containing various thiophenecarboxylate and related ligands, $Co(NH_3)_5L^{2+}$ (Figure 1). Each of the ligands L has a five-membered heterocyclic ring containing a sulfur atom, Co(III) being coordinated to a carboxylate group which is bound to the ring via a variety of carbon linkages (Figure 1). The redox center can therefore be linked to the electrode surface by a varying number of conjugated and/or saturated bonds. The homogeneous inner-sphere reductions of closely related carboxylate complexes have also been studied extensively.[6] An important virtue of these systems is that they are closely related to the bipyridine-bridged homogeneous intramolecular reactions featuring Co(III) reduction that have received extensive recent scutiny.[1d,f-h] The detailed comparisons of rate parameters that can be made for reactants with systematically varying bridging ligand structures largely circumvent the lack of redox thermodynamic information resulting from the chemical irreversibility of the Co(III)/(II) couple.

Although the heterocyclic sulfur is only weakly basic,[7] sufficiently strong adsorption of the thiophene complexes typically occurs to enable their electroreduction kinetics within the adsorbed state to be obtained directly by using rapid linear sweep voltammetry. Such measurements at mercury, gold, and copper surfaces are described here, along with corresponding adsorption data at mercury electrodes. Electrochemical kinetics data are also reported for several related Co(III) carboxylates, along with kinetics data for the homogeneous outer-sphere reduction of the thiophene- and related carboxylate complexes by $Ru(NH_3)_6^{2+}$. Taken together, the results demonstrate the role of bond conjugation in promoting heterogeneous electron transfer via extended organic bridges.

Experimental Section

Materials. Eight of the nine thiophenecarboxylate ligands and all three furoate ligands used here (Figure 1) were obtained from Aldrich Co. 2-Thiophenepropionic acid was prepared by hydrogenation of 2-thiopheneacrylic acid over a 5% palladium-activated carbon catalyst in ether solution at room temperature under 130 psi hydrogen pressure. Its structure was verified by mass spectrometry and NMR. The mass spectrum (70 EV) has a parent peak at *m/e* 156; the ^1H NMR ($CDCl_3$, 25 °C) has δ 2.73 (t, 2 H), 3.16 (t, 2 H), 6.83 (s, 1 H), 6.90 (t, 1 H), 7.10 (d, 1 H), 8.05 (s, 1 H) (relative to Me_4Si).

The general procedure used to synthesize the various carboxylatopentaamminecobalt(III) complexes involved a modification of that described in ref 6a. Typically 20 mmol of the organic acid with 10 mL of 1.75 M NaOH was heated at 80 °C for 10 min and then filtered. To the filtrate was added 1.0 g of aquopentaamminecobalt(III) perchlorate in 2 mL of hot water. The mixture was kept at 55 °C with stirring for 48 h in an oil bath. The solution was then cooled to room temperature and added to a larger separatory funnel containing 5 mL of water, 2.0 mL of 9 M $HClO_4$, and 150 mL of ether. The funnel was shaken for 5 min, the ether layer decanted, and the aqueous layer extracted with another two 150-mL aliquots of ether; 10 mL of 9 M $HClO_4$ was added to the aqueous solution and the solution cooled to −10 °C. The precipitated complexes were purified chromatographically using Biogel P-2 (Biorad Corp.), eluting with water, and then recrystallized from water as the perchlorate salts. The purity of the resulting compounds was verified by microanalysis. These were performed by the Microanalytical Laboratory at Purdue University. Percentages of N, C, S, and H agreed within 0.4% of the expected values.

The sodium perchlorate supporting electrolyte was obtained either from G. F. Smith or prepared from sodium carbonate and perchloric acid, and twice recrystallized from water. All solutions were prepared using water that was purified by double distillation from alkaline permanganate.

Electrochemical and Homogeneous Kinetics Measurements. Apparent electrochemical rate constants, k_{app}, for the overall reduction of the Co(III) complexes were determined at mercury, gold, and copper electrodes by using normal pulse polarography as described in ref 4 and 8. Bulk reactant concentrations, C_b, from 0.1–1 mM were typically employed. Rotating disk voltammetry was additionally used to determine k_{app} at the solid surfaces.[4] A dropping mercury electrode (DME) having a mechanically controlled drop time of 2 s was used to determine k_{app} at mercury. The gold and copper electrodes were of a rotating disk construction, and were mechanically polished with 0.3 μm alumina on a polishing wheel immediately before use. Rate constants, k_{et}, for reduction of the adsorbed Co(III) complexes were obtained by means of rapid linear sweep voltammetry.[3b,9] [As for the reduction of diffusing Co(III) reactant, no corrections for anodic back reactions were required since the cobalt complexes rapidly dissociate upon reduction.[4,10]] These measurements utilized a hanging mercury drop or stationary gold or copper electrodes. Potential sweeps were made by means of a PAR 173 potentiostat and a PAR 175 potential programmer, and the current–potential transients were recorded with a Nicolet Explorer I oscilloscope coupled to a Houston 2000 X–Y recorder. The data analysis method is described in the Results section.

This technique was also employed to determine the extent of adsorption at the initial potential. However, more extensive information on the adsorption thermodynamics at hanging mercury drop electrodes was obtained using single-step chronocoulometry. A microcomputer-controlled data acquisition and analysis system was used for these measurements.[4] Initial potentials between ca. 200 and 0 mV vs. SCE were employed, with C_b between ca. 0.01 and 1 mM. Chronocoulometric potential steps were selected so that the final potential was sufficiently negative (usually beyond −500 mV vs. SCE) so as to minimize complications from adsorption of the thiophene ligands set free upon Co(III) reduction.[11-13]

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(6) (a) Gould, E. S.; Taube, H. *J. Am. Chem. Soc.* **1964**, *1318*. (b) Fan, F. R.; Gould, E. S. *Inorg. Chem.* **1974**, *13*, 2639.

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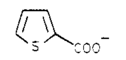
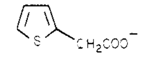
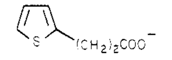
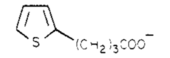
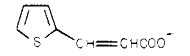
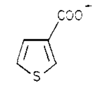
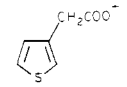
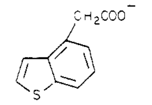
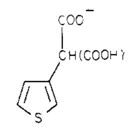
(9) Guyer, K. L.; Barr, S. W.; Weaver, M. J. In "Proceedings of the Symposium on Electrocatalysis"; O'Grady, W. E., Ross, P. N., Jr., Will, F. G., Eds.; The Electrochemical Society: Pennington, NJ, 1982; p 377.

(10) Satterberg, T. L; Weaver, M. J. *J. Phys. Chem.* **1978**, *82*, 1784.

(11) From an analysis of the potential dependence of the adsorption thermodynamics as described in ref 12, the "electrosorption valency", $(1/F)(\partial q^m/\partial\Gamma)_E$, for the present systems was determined to be quite small, ca. 0.1. This implies that only a small fraction (ca. 10%) of the measured current for reduction of the adsorbed reactant is nonfaradaic in origin.[12]

Table I. Unimolecular Rate Constants for Adsorbed $Co^{III}(NH_3)_5L$ Electroreduction and Related Adsorption and Kinetic Data. at 0 mV vs. SCE at 24 °C in 0.1 M $NaClO_4$ + 5 mM $HClO_4$

	ligand L	surface	K_p^H,[a] cm	k_{et},[b] s^{-1}	α_{et}[c]	A_{et},[d] s^{-1}	k_{app},[e] cm s^{-1}	α_{app}[f]	k_{et}^{est},[g] s^{-1}
I		Hg	3×10^{-5}	25	~0.6		1.8×10^{-3}	0.71	60
		Au		3 (10)	0.6		7×10^{-5}		
II		Hg	4×10^{-4}	2.2	0.6	$\sim 1 \times 10^{10}$	4.5×10^{-4}	0.75	4.5
		Au		5 (3)	0.6		1.2×10^{-5}		
III		Hg	2.5×10^{-4}	2.5	0.6	$\sim 3 \times 10^{10}$	6.3×10^{-4}	0.65	5
		Au		6 (2)	0.6		1.8×10^{-5}		
		Cu		0.3 (4)	0.6				
IV		Hg	1.5×10^{-4}	2.0	0.6	$\sim 1 \times 10^{9}$	3.2×10^{-4}	0.57	4
		Au		3 (7)	0.55		1.3×10^{-5}		
		Cu		0.9 (4)	0.55				
V		Hg	9×10^{-5}	45	0.6	$\sim 2 \times 10^{12}$	2.8×10^{-3}	0.62	50
		Au		6 (1)	0.6		2×10^{-5}		
VI		Hg	2.5×10^{-5}	20	~0.6		1.7×10^{-3}	0.72	70
		Au		3 (8)	0.65		7.5×10^{-5}		
VII		Hg	3×10^{-4}	1.5	0.6		4.9×10^{-4}	0.79	3
		Au		10 (6)	0.5		3×10^{-5}		
VIII		Hg	5.5×10^{-4}	1.0	0.6		2.7×10^{-4}	0.67	1.5
		Au		2 (6)	0.6		2×10^{-5}		
IX		Hg	1.8×10^{-4}	2	0.65		2.6×10^{-4}	0.63	2.5
		Au		1.5 (4)	0.6		4×10^{-5}		
		Cu		~1.0 (4)	0.6				

[a] Equilibrium constant for formation of adsorbed reactant at mercury, obtained using chonocoulometry for sufficiently small adsorbate surface concentrations so that Henry's law applies (see text). [b] Unimolecular rate constant for reduction of surface-attached $Co^{III}(NH_3)_5L$ complex, obtained in the text. Values in parentheses following entries for gold and copper are reactant surface concentrations Γ (in units of 10^{11} mol cm^{-2}) at which values of k_{et} were obtained. [c] Transfer coefficient for surface-attached reactant, obtained from $\alpha_{et} = -(RT/F)\cdot(\partial \ln k_{et}/\partial E)_{\Gamma}$. [d] Unimolecular frequency factor, obtained from electrochemical activation parameters for reduction of surface-attached reactant (see text and ref 25 for details). Estimated uncertainties in A_{et} are ca. five-fold, due to uncertainties in estimation of entropic driving force.[25] [e] Apparent rate constant for overall electrochemical reaction, using normal pulse polarography with bulk reactant concentration equal to 0.8 mM. [f] Apparent transfer coefficient, from $\alpha_{app} = (-RT/F)(\mathrm{d} \ln k_{app}/\mathrm{d}E)$. [g] Unimolecular rate constant for surface-attached reactant, estimated from values of k_{app} and K_p using eq 1. (Values of K_p employed for this purpose are formal values obtained at appropriate bulk reactant concentrations by using chronocoulometry. In some cases, these differ somewhat from listed values of K_p^H which refer to small adsorbate coverages where Henry's law applies.)

Rate constants, k_{Ru}, for the homogenous reduction of the Co(III) complexes by $Ru(NH_3)_6^{2+}$ were determined using a polarographic method. This entailed monitoring the concentration of $Ru(NH_3)_6^{2+}$ as a function of time from the d.c. polarographic current for $Ru(NH_3)_6^{2+}$ electrooxidation following the addition of an excess of the Co(III) oxidant. Typically the initial $Ru(NH_3)_6^{2+}$ concentration was ca. 1 mM, and the Co(III) concentrations was 10 mM so that the reaction kinetics were approximately pseudo first order. Mixtures of sodium trifluoroacetate and trifluoroacetic acid (5–20 mM) were employed as the background electrolyte, having a total concentration of 0.05 M. The $Ru(NH_3)_6^{2+}$ reactant was generated from $Ru(NH_3)_6^{3+}$ by electroreduction of 2 mL solution in trifluoroacetate media at a stirred mercury pool at −600 mV vs. SCE. The homogeneous reaction was initiated by injecting 2 mL of a deaerated solution of the desired Co(III) complex.

The $Ru(NH_3)_6^{3+}$ solution was prepared from $Ru(NH_3)_6 \cdot Cl_3$ (Matthey Bishop), purified as described in ref 14. The Co(III) solution was prepared by dissolving the solid perchlorate salt in water and eluting through an anion-exchange column (BioRad AG1-X10) charged with trifluoroacetate ions in order to remove the oxidizing perchlorate ions. The polarographic current was monitored at a potential (usually 100 mV vs. SCE) where the $Ru(NH_3)_6^{2+}$ electrooxidation is diffusion controlled, and yet Co(III) electroduction occurs at a negligible rate so that the observed current is directly proportional to the remaining $Ru(NH_3)_6^{2+}$ concentration in homogeneous solution. The half-lives of the present reactions are typically 15–60 min. This technique was found to yield essentially identical rate constants for the $Co(NH_3)_5OAc^{2+}$–$Ru(NH_3)_6^{2+}$ reaction (OAc = acetate) as obtained by the conventional spectrophotometric method.[14]

All electrode potentials are quoted with respect to the saturated calomel electrode (SCE). All kinetics and adsorption measurements were made at 24 ± 0.5 °C.

Results

Normal pulse polarography of the nine thiophenepentaamminecobalt(III) complexes (I–IX, Figure 1) at the DME in 0.1 M $NaClO_4$ each yielded a single reduction wave within the potential region ca. 50 to −200 mV, which was pH independent in the range pH 2–7. Chronocoulometric measurements indicated that most of these complexes are strongly adsorbed, at least in the potential region 200 to 0 mV where little or no cathodic current flowed. Generally, at a given bulk concentration, C_b, the adsorbate surface concentration, Γ, decreased gradually as the potential was made more negative. A saturation value of Γ, Γ_s, around 8 to 12 × 10^{-11} mol cm^{-2} was obtained for sufficiently strongly adsorbed complexes from the limiting plateau region of the adsorption isotherm.[12] Values of the "adsorption coefficient", $K_p^H = \Gamma/C_b$, determined at 0 mV under Henry's law conditions, i.e., for values of Γ sufficiently less than Γ_s so that $\Gamma \propto C_b$, are listed for each adsorbate in Table I. This quantity equals the equilibrium constant for forming the "precursor state" from the bulk reactant

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(12) (a) Weaver, M. J.; Anson, F. C. *J. Electroanal. Chem.* **1975**, *58*, 95. (b) Weaver, M. J.; Anson, F. C. *Ibid.* **1975**, *60*, 19.

(13) The adsorption thermodynamics of the Co(III) thiophene complexes will be discussed in more detail elsewhere.

(14) Pladziewicz, J. R.; Meyer, T. J.; Broomhead, J. A.; Taube, H. *Inorg. Chem.* **1973**, *12*, 639.

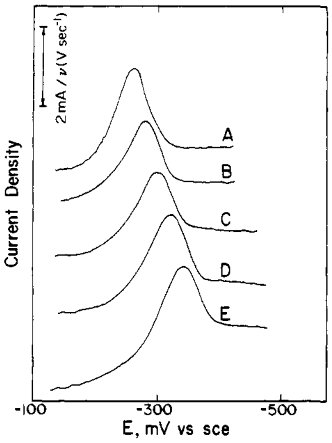

Figure 2. Cathodic linear sweep voltammograms for reduction of adsorbed 2-thiopheneacetatopentaamminecobalt(III) [II, Figure 1]. Bulk reactant concentration = 60 μM; initial surface concentration = 3 × 10^{-11} mol cm^{-2}. Current density (y axis) scale shown is 2 mA/ν where ν is sweep rate in V s^{-1}. Key: A, 5 V s^{-1}; B, 10 V s^{-1}; C, 20 V s^{-1}; D, 50 V s^{-1}; E, 100 V s^{-1}.

(vide infra). (Although to an extent arbitrary, the value 0 mV vs. SCE was chosen as a common potential for the comparison of the adsorption and various kinetic data gathered in Table I in order to minimize the extent of data extrapolation that was necessarily involved).

Fast linear sweep voltammograms for the reduction of these adsorbed complexes exhibited symmetrical peaks in the potential region ca. −100 to −300 mV. A typical series of voltammograms obtained with sweep rates of 5, 10, 20, 50, and 100 V s^{-1} is shown in Figure 2. The adsorbate surface concentration, Γ_i, at the initial potential can be found simply from the charge density, q_f, contained under the voltammetric peak using $\Gamma_i = q_f/F$, providing that sufficiently dilute bulk reactant concentrations (ca. 50 μM) and rapid sweep rates ($\geq$5 V s^{-1}) were employed so that the faradaic current was due almost entirely to reduction of initially adsorbed, rather than diffusing, reactant.[3b,9] This circumstance was confirmed by the independence of q_f to the sweep rate. (On this basis only the voltammogram in Figure 2 obtained at 5 V s^{-1} contains a significant contribution from the diffusing reactant.) Good agreement was generally obtained for values of Γ_i obtained using linear sweep voltammetry and chronocoulometry. In one respect, the latter technique is of broader applicability since relatively accurate values of Γ_i (within ca. 1 to 2 × 10^{-11} mol cm^{-2}) can be obtained even for bulk concentrations up to a few millimolar. However, we have found single-step chronocoulometry to be of little utility at several solid surfaces for monitoring transition-metal adsorption induced by inorganic ligands.[3,9] Similar difficulties were encountered with the present complexes at gold and copper electrodes. Nevertheless, the thiophenecarboxylate complexes were sufficiently strongly adsorbed at these surfaces to enable their adsorption to be determined by rapid linear sweep voltammetry. Adsorption measurements using the latter technique were also attempted at silver and platinum surfaces, but were thwarted by the onset of silver dissolution and/or the lack of well-defined voltammograms.

Rate parameters for the reduction of adsorbed Co(III) complexes were obtained from the linear sweep voltammograms as follows. Unimolecular rate constants, k_{et}^{E}, corresponding to a series of reactant surface concentrations, Γ_r^E, and electrode potentials, E, were obtained at various points on a given voltammetric wave by using the relation[9,12] $k_{et}^{E} = i_f^E/F\Gamma_r^E$, where i_f^E is the faradaic current density at that potential. The values of i_f^E were obtained by subtracting the nonfaradaic background current, estimated by interpolating the current baseline on either side of the voltammetric wave, from the total current.[3b,9,11] The corresponding values of Γ_r^E were obtained from the faradaic charge density required to reduce the adsorbate remaining at that point. The potential dependence of k_{et} at each value of Γ_r, expressed as a transfer coefficient α_{et} [$=-(RT/F)(\partial \ln k_{et})/\partial E)_\Gamma$], was determined from the corresponding slope of a plot of the voltammetric peak potential against log ν, for variation in the sweep rate, ν, between 10 and 100 V s^{-1}.[16]

Values of k_{et}, evaluated for E = 0 mV vs. SCE, along with the corresponding values of α_{et} resulting from this analysis are listed in Table I. These rate parameters at mercury electrodes were determined for values of Γ_r in the range ca. 1 to 5 × 10^{-11} mol cm^{-2}. The values of k_{et} were found to be essentially independent of Γ_r under these conditions; i.e., the kinetics were approximately first order in the adsorbed reactant. Less straightforward behavior was encountered at gold and copper surfaces where the derived values of k_{et} were found to depend on Γ_r as well as potential. This behavior appears to be typical at polycrystalline solid surfaces, and is associated with linear sweep voltammetric peaks that are unexpectedly broad.[3,9] Nevertheless, the values of α_{et} obtained from the dependence of the voltammetric peak potentials upon scan rate were consistently similar, ca. 0.6, to those observed at mercury (Table I) so that relative values of k_{et} for almost all these systems will be largely independent of the electrode potential chosen for comparison. Consequently, approximate values of k_{et} determined at gold and copper surfaces for 0 mV (Table I) were obtained by extrapolating the values obtained for potentials in the vicinity of the voltammetric peak currents using these values of α_{et}. Since the values of k_{et} were somewhat dependent upon the reactant surface concentration, the approximate values of Γ_r at which the listed value of k_{et} was determined are also given (in units of 10^{11} mol cm^{-2}) alongside in parentheses in Table I. All the values of k_{et} determined at mercury, gold, and copper surfaces were found to be essentially independent of pH in the region 2–7.

Table I also contains indirectly determined ("estimated") values of k_{et}, k_{et}^{est}, for reduction of the thiophenecarboxylate complexes at mercury. These were obtained from the apparent rate constants, k_{app} (i.e., those obtained for the overall electrochemical reaction), extracted from the normal pulse polarograms at 0 mV together with the corresponding adsorption coefficients, K_p, obtained from chronocoulometry, by using the relation[3,17]

$$k_{et}^{est} = k_{app}/K_p \qquad (1)$$

Since the values of k_{app} given in Table I were obtained for a bulk reactant concentration C_b of 0.8 mM, the values of K_p used were those derived from the relation K_p(cm) = $\Gamma_{0.8}$ (mol cm^{-2})/8 × 10^{-7} (mol cm^{-3}), where $\Gamma_{0.8}$ is the surface reactant concentration at 0 mV corresponding to this bulk concentration. (For a few reactions in Table I, somewhat smaller bulk reactant concentrations are involved because of the occurrence of significant reactant diffusion polarization at 0 mV.) The corresponding values of k_{et} and k_{et}^{est} in Table I are in reasonable agreement, thereby confirming the applicabilty of the preequilibrium model upon which eq 1 is based.[17]

Table I also lists values of k_{app} at gold, also for C_b = 0.8 mM, determined using normal pulse polarography and rotating disk voltammetry. Reaction orders, obtained using the latter technique by monitoring the response of the voltammetric current to variations in the rotation speed,[18,19] were typically close to zero. Corresponding estimates of k_{et}^{est} are not given in Table I since sufficiently accurate values of K_p were not obtained.

Apparent rate constants were also obtained at mercury electrodes for three furan analogues X, XI, and XII, of the thiophene complexes I, VI, and V, respectively (Figure 1). Values of k_{app}

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(15) Fan, F-R F.; Gould, E. S. *Inorg. Chem.* **1974**, *13*, 2647.

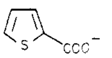
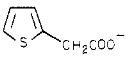
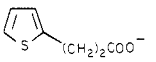
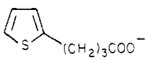
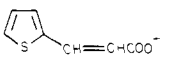
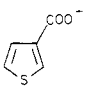
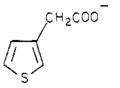
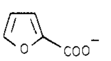
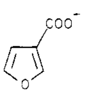
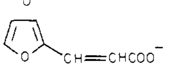
(16) Angerstein-Kozlowska, H.; Klinger, J.; Conway, B. E. *J. Electroanal. Chem.* **1977**, *75*, 45.

(17) Hupp, J. T.; Weaver, M. J. *J. Electroanal. Chem.* **1983**, *152*, 1.

(18) Some of the values of K_p used for this purpose are significantly smaller than the corresponding values of the K_p^H listed in Table I; this is due to the approach of saturation coverage for some reactants under the higher bulk concentrations at which the pulse polarographic values of k_{app} were obtained. As expected,[3a,19] the corresponding values of the apparent electrochemical reaction orders were significantly below unity under these conditions; i.e., the values of k_{app} decreased with increasing bulk reactant concentration.

(19) Guyer, K. L.; Barr, S. W.; Cave, R. J.; Weaver, M. J. In "Proceedings of the 3rd Symposium on Electrode Processes"; Bruckenstein, S., McIntyre, J. D. E., Miller, B., Yeager, E., Eds.; Electrochemical Society: Pennington, NJ, 1980; p 390.

Table II. Comparison of Rate Parameters for Reduction of Selected $Co^{III}(NH_3)_5L$ Complexes at Mercury Electrodes at 0 mV vs. SCE and in Homogeneous Solution

ligand L	k_{et},[a] s^{-1}	k_{et}/k_{et}^{Ac} [b]	k_{app}/k_{app}^{Ac} [c]	k_{Ru},[d] M^{-1} s^{-1}	k_{Ru}/k_{Ru}^{Ac} [f]	k_{Cr}/k_{Cr}^{Ac} [g]
CH_3COO^-	(~50)			0.018, 0.022[e]		
	25	0.5	900	0.013	0.7	0.85[h]
	2.2	0.05	230	0.035	1.9	
	2.5	0.05	320	0.035	1.9	
	2.0	0.04	160	0.011	0.6	
	45	0.9	1400	0.041	2.3	
	20	0.4	850	0.013	0.7	0.75[h]
	1.5	0.03	250	0.018	1.0	
			110	0.019	1.1	1.1[i]
			65	0.012	0.7	
			550	0.019	1.1	3.9[j]

[a] Unimolecular rate constant for surface-attached reactant at mercury in 0.1 M $NaClO_4$ + 5 mM $HClO_4$ (from Table I). Value given in parentheses for acetate complex is estimated for outer-sphere pathway as described in the text. [b] Ratio of k_{et} for given complex to corresponding estimated value for L = CH_3COO^-. [c] Ratio of apparent rate constant for given complex (Table I) to that for L = CH_3COO^- in 0.1 M $NaClO_4$ + 5 mM $HClO_4$; k_{app}^{OAc} = 2 × 10^{-6} cm s^{-1}. [d] Second-order rate constant for homogeneous reduction of given complex by $Ru(NH_3)_6^{2+}$. Except where noted, electrolyte was 0.05 M sodium trifluoroacetate–trifluoroacetic acid mixture containing 5-20 mM acid. (Rate constants were acid-independent within this range.) See text for details. [e] Determined in 0.5 M LiCl containing 0.013 M H^+; from ref 6b. [f] Ratio of rate constant for reduction of given complex by $Ru(NH_3)_6^{2+}$ to that for L = CH_3COO^-. [g] Ratio of rate constant for reduction of given complex by Cr^{2+} to that for L = CH_3COO^- under similar conditions. Data sources: [h] References 6a and 15. [i] Reference 15. [j] Reference 6b.

for X, XI, and XII equal to 2.2 × 10^{-4}, 1.3 × 10^{-4}, and 1.1 × 10^{-3} s^{-1}, respectively, were obtained in 0.1 M $NaClO_4$ + 5 mM $HClO_4$ at 0 mV. Note that these rate constants are ca. 3- to 10-fold smaller than those for the corresponding thiophene complexes (Table I). In contrast to the thiophenes, the adsorption of these furan complexes could not be detected at mercury electrodes, so that only an upper limit for K_p^H, $\lesssim 1 \times 10^{-5}$ cm, could be established.

A summary of rate constants, k_{Ru}, for the homogeneous reduction of the thiophene and several related carboxylate complexes, $Co(NH_3)_5L^{2+}$, by $Ru(NH_3)_6^{2+}$ is given in Table II. The values of k_{Ru} were found to be essentially acid independent for $[H^+] \approx$ 5–20 mM.

Discussion

The electrochemical reduction data for the various Co(III) thiophene complexes at mercury electrodes given in Table I display a marked sensitivity to the structure of the bridging thiophene ligand. In particular, the addition of one or more CH_2 groups between the thiophene ring and the carboxylate group results in substantially (10- to 20-fold) smaller values of k_{et} (Table I). Nevertheless, the presence of an ethylenic linkage in the carboxylate side chain (compound V), thereby maintaining bond conjugation between the carboxylate and thiophene groups, yields a value of k_{et} (45 s^{-1}) slightly larger than those for the 2- and 3-thiophenecarboxylates (I, VI; 25 and 20 s^{-1}, respectively). The absence of detectable adsorption for the furan analogues confirms the expectation that the thiophene complexes are indeed bound to the surface via the heterosulfur atom.

It therefore appears that the presence of bond conjugation between the thiophene sulfur and carboxylate oxygens that are bound to the mercury surface and Co(III), respectively, noticeably facilitates heterogeneous electron transfer to the cobalt center. (Note that the thiophene ring itself possesses considerable aromatic character as a result of donation of a sulfur lone pair to the π-electron ring system.[20]) These findings bear a close resemblence to some recent results for electron mediation within some binuclear complexes. Thus Taube and co-workers found that the interposition of a CH_2 group between the pyridyl rings in 4,4′-bipyridine slowed by ca. 20-fold the intramolecular electron-transfer rate between Co(III) and Ru(II) centers bound to the ring nitrogens.[2f,g,21] Also, interposing an ethylenic linkage between the aromatic rings diminishes k_{et} by only ca. 2-fold, whereas k_{et} for the corresponding ethane derivative is ca. 20-fold smaller.[2f,g,21] Nevertheless, as for the present systems, the addition of a second CH_2 group has little further influence upon k_{et}.[2f,g,21] More marked decreases in k_{et} have been observed for the intramolecular reduction of carboxylatopentamminecobalt(III) by a nitrobenzoato radical upon the interposition of saturated linkages.[22]

These rate variations are reasonably ascribed, at least in part, to decreases in the electronic coupling between the redox centers brought about by an interrruption of the π-electron delocalization within the bridging group. Such diminished electronic coupling would seem most likely to affect k_{et} via decreases in the probability of electron tunneling, κ_{el}, once the appropriate nuclear configu-

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[20] See, for example: Albert, A.; "Heterocyclic Chemistry"; Athlone Press: London, 1968; Chapter 6.

[21] (a) Fischer, F.; Tom, G. M.; Taube, H. *J. Am. Chem. Soc.* **1976**, *98*, 5512. (b) Zawacky, S. K. S.; Taube, H. *J. Am. Chem. Soc.* **1981**, *103*, 3379.

[22] Whitburn, K. D.; Hoffman, M. Z.; Simic, M. G.; Brezniack, N. V. *Inorg. Chem.* **1980**, *19*, 3180.

ration of the reactants has been attained (i.e., to increasingly nonadiabatic pathways). Such a conclusion has indeed been made for the homogeneous systems on this basis.[1f] Several other factors may nevertheless be responsible for such rate variations, as now will be considered.

According to contemporary treatments of electron transfer, the measured unimolecular rate constant can be expressed as[3,17,23]

$$k_{\mathrm{et}} = \kappa_{\mathrm{el}}\nu_{\mathrm{n}} \exp(-\Delta G^{*}_{\mathrm{et}}/RT) \tag{2a}$$

where

$$\Delta G^{*}_{\mathrm{et}} = \Delta G^{*}_{\mathrm{int}} + \alpha_{\mathrm{et}}[F(E - E^{\circ}) + RT(\ln K_{\mathrm{p}} - \ln K_{\mathrm{s}})] \tag{2b}$$

Equation 2a relates the rate constant for the elementary electron-transfer step, k_{et}, to the free energy of reorganization, $\Delta G^{*}_{\mathrm{et}}$, where ν_{n} is the nuclear frequency factor for this step, ca. 1×10^{13} s^{-1}.[17] In eq 2b, $\Delta G^{*}_{\mathrm{et}}$ is divided into a so-called "intrinsic" component, $\Delta G^{*}_{\mathrm{int}}$, and a "thermodynamic" component given within the brackets; E° is the standard potential for the redox couple involved, and K_{p} and K_{s} are the equilibrium constants for forming the precursor and successor ground states from the bulk reactant and product, respectively.[24] An identical relationship applies to homogeneous redox processes, only with the homogeneous free-energy driving force, $-\Delta G^{\circ}$, replacing $F(E - E^{\circ})$. The intrinsic barrier $\Delta G^{*}_{\mathrm{int}}$ is the free-energy barrier that would remain if the free-energy driving force for the elementary step equalled zero; the component of this latter term, $(\ln K_{\mathrm{p}} - \ln K_{\mathrm{s}})$, in eq 2b corrects for any changes in the driving force for the overall reaction, $F(E - E^{\circ})$, resulting from binding the reactant to the electrode surface.

Variations in k_{et} caused by structural alterations in the organic bridging ligand may arise from changes in $\Delta G^{*}_{\mathrm{int}}$, E°, and $(\ln K_{\mathrm{p}} - \ln K_{\mathrm{s}})$ as well as in κ_{el}. Although E° for the present Co(III)/(II) couples cannot be determined owing to the substitution lability and instability of Co(II), any significant variations in E° and also in $\Delta G^{*}_{\mathrm{int}}$ within a series of $\mathrm{Co(NH_3)_5L^{2+}}$ complexes can be detected by examining the relative rates of reduction using $\mathrm{Ru(NH_3)_6^{2+}}$. This is because for such outer-sphere reactions structural variations in L may influence k_{et} only through inductive effects at the cobalt redox center, thereby altering E° and possibly $\Delta G^{*}_{\mathrm{int}}$. The remaining terms in eq 2, K_{p}, K_{s}, and κ_{el}, should remain approximately constant since the carboxylate group L should not be involved directly in electron mediation. Inspection of the rate constants for $\mathrm{Ru(NH_3)_6^{2+}}$ reduction, k_{Ru}, given in Table II reveals that only minor ($\lesssim$3-fold) differences in k_{Ru} are seen between the various Co(III) thiophene complexes. Moreover, no significant differences in k_{Ru} are seen between those thiophene or furan complexes featuring ligand conjugation and those containing methylene linkages in the side chain. These data are also presented in Table II as rate ratios, $k_{\mathrm{Ru}}/k_{\mathrm{Ru}}^{\mathrm{Ac}}$, with respect to the rate constant, $k_{\mathrm{Ru}}^{\mathrm{Ac}}$, for the $\mathrm{Ru(NH_3)_6^{2+}}$ reduction of the acetate complex $\mathrm{Co(NH_3)_5OAc^{2+}}$. Corresponding rate ratios for $\mathrm{Cr(OH_2)_6^{2+}}$ reduction, $k_{\mathrm{Cr}}/k_{\mathrm{Cr}}^{\mathrm{Ac}}$, obtained from literature data, are also listed in Table II. Although these latter data refer to inner-sphere pathways featuring binding of Cr(II) to the carbonyl oxygen, the values of $k_{\mathrm{Cr}}/k_{\mathrm{Cr}}^{\mathrm{Ac}}$ display a similar insensitivity to the nature of the carboxylate ligand. (Note that the thiophene ring and carbon linkage assume a pendant position for Cr(II) reduction,[1a] rather than directly linking the donor and acceptor sites as in the heterogeneous inner-sphere pathways.)

These results therefore suggest that the observed sensitivity of k_{et} for Co(III) thiophene reduction at mercury to the bridging ligand structure is due to variations in κ_{el} and/or the "surface thermodynamic" term $(\ln K_{\mathrm{p}} - \ln K_{\mathrm{s}})$ rather than to variations in E° or $\Delta G^{*}_{\mathrm{int}}$. Although values of K_{s} are unknown in view of the instability of the Co(II) successor state, the likely dependence of $(\ln K_{\mathrm{p}} - \ln K_{\mathrm{s}})$ upon the bridging ligand structure can be deduced from the corresponding measured variations in K_{p} (Table I). It is seen that K_{p} is ca. 3- to 10-fold smaller for the conjugated thiophenes than for those containing one or more $\mathrm{CH_2}$ groups between the ring and carboxylate groups. These differences can be understood in terms of electron withdrawal from the sulfur atom by Co(III). Such electron polarization will be aided by bond conjugation, giving rise to weaker sulfur–mercury binding and thereby accounting for the smaller values of K_{p} for these systems (Table I). Quantitatively similar, yet milder, variations in K_{s} would be expected in view of the smaller charge and weaker coordinate binding with Co(II). Since these variations in K_{s} are liable to partly cancel those in K_{p}, a reasonable upper limit to the variations in $(\ln K_{\mathrm{p}} - \ln K_{\mathrm{s}})$ with bridging ligand structure is provided by the variations in $\ln K_{\mathrm{p}}$ themselves. In view of eq 2, since $\alpha_{\mathrm{et}} \approx 0.6$ (Table I), to entirely account for the observed ca. 20-fold variations in terms of this "thermodynamic" contribution would require at least 40-fold variations in K_{p}. This is clearly much larger than are observed.

We therefore deduce that the smaller values of k_{et} at mercury electrodes resulting from interruption of bond conjugation in the organic mediating group are due predominantly to decreases in the electronic transmission coefficient κ_{el} rather than to increases in the reorganization energy $\Delta G^{*}_{\mathrm{et}}$ (eq 2). Support for this conclusion is obtained from the corresponding activation parameters. Approximate estimates of $\kappa_{\mathrm{el}}\nu_{\mathrm{n}}$ were extracted from the measured Arrhenius frequency factors for several of the Co(III) thiophene reactants at mercury by correcting for the entropic driving force.[25,26] The resulting values of $\kappa_{\mathrm{el}}\nu_{\mathrm{n}}$, labeled A_{et}, for one conjugated and three nonconjugated Co(III) thiophene reactants, taken from ref 25, are also given in Table I. Note that A_{et} for the conjugated reactant V, ca. 2×10^{12} s^{-1}, is close to that expected (1×10^{13} s^{-1}) if $\kappa_{\mathrm{el}} \sim 1$.[25] The corresponding values of A_{et} for the three nonconjugated reactants II–IV, are 10^{2}–10^{3}-fold smaller, mirroring the corresponding smaller values of k_{et} for these latter reactants (Table I), as expected if these rate decreases are due predominantly to decreases in κ_{el}.

Further insight into the factors influencing electron mediation by the bridging ligands can be obtained by comparing the observed values of k_{et} (s^{-1}) with those obtained for structurally related reactants following *outer-sphere* pathways.[3a] Such values of k_{et} can be estimated from the work-corrected outer-sphere rate constants $k_{\mathrm{cor}}^{\mathrm{os}}$ using[3a,17]

$$k_{\mathrm{et}} = k_{\mathrm{cor}}^{\mathrm{os}}/\delta r \tag{3}$$

where δr is the effective thickness of the "reaction zone" adjacent to the electrode surface which forms the effective outer-sphere precursor state.[17]

Values of k_{app} corresponding to outer-sphere pathways are unknown for the Co(III) thiophene complexes. The furan analogues (Figure 1, Table II) also appear to react via "ring-mediated" pathways on the basis of the values of k_{app} that are only marginally (ca. 3- to 10-fold) less than those for the Co(III) thiophenes (Table I). However, $\mathrm{Co(NH_3)_5OAc^{2+}}$ provides a suitable reactant likely to react via an outer-sphere pathway since it lacks a suitable surface binding group. Moreover, the rate constant for reduction of this complex by $\mathrm{Ru(NH_3)_6^{2+}}$ is virtually the same as those for the Co(III) thiophenes (Table II), to that the outer-sphere electrochemical pathways should have similarly close values of k_{et}.[3a,28] From the experimental value of $k_{\mathrm{cor}}^{\mathrm{os}}$ for $\mathrm{Co(NH_3)_5OAc^{2+}}$ reduction at 0 mV at mercury, 1×10^{-6} cm s^{-1},[29] and assuming that $\delta r \sim 2$ Å,[31] from eq 3 $k_{\mathrm{et}} \sim 50$ s^{-1} at 0 mV. Although this estimate

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[23] Weaver, M. J. *Inorg. Chem.* **1979**, *18*, 402.

[24] The equilibrium constants K_{p} and K_{s} given in eq 2b need not refer to sufficiently small surface coverages so that Henry's law applies, although the interpretation of the unimolecular rate parameters in terms of eq 2a and 2b is the most straightforward under these conditions.

[25] Li, T. T.-T.; Guyer, K. L.; Barr, S. W.; Weaver, M. J. *J. Electroanal. Chem.*, in press.

[26] The fundamental virtues of electrochemical activation parameter measurements with surface-attached reactants have also been described recently.[27]

[27] Hupp, J. T.; Weaver, M. J. *J. Electroanal. Chem.* **1983**, *145*, 43.

[28] Barr, S. W.; Guyer, K. L.; Li, T. T-T.; Liu, H. Y.; Weaver, M .J. In "The Chemistry and Physics of Electrocatalysis"; McIntyre, J. D. E., Weaver, M. J., Yeager, E., Eds.; Electrochemical Society: Pennington, NJ, in press.

[29] This value is obtained from the experimental apparent rate constant, $k_{\mathrm{app}} \approx 2 \times 10^{-6}$ cm s^{-1} in 0.1 M $\mathrm{NaClO_4}$ (T. T.-T. Li, unpublished data) after a small work-term correction is applied as described in ref 30.

of k_{et} may be as much as two- to three-fold in error, it is interesting to note that it is similar to the values of k_{et} for the conjugated Co(III) thiophenes (30–50 s^{-1}) but substantially larger than those for the nonconjugated reactants (2–2.5 s^{-1}) (Tables I and II). [The very large rate ratios k_{app}/k_{app}^{Ac} listed in Table II can therefore be accounted for in terms of differences in precursor stabilities between the inner- and outer-sphere pathways.] This therefore suggests that binding the latter reactants to the electrode surface constrains them to react via a less favorable, presumably more nonadiabatic (smaller κ_{el}), pathway than is available to either the unadsorbed reactant or Co(III) bound to the surface via a conjugated organic bridge.

When the "conduction pathway" provided by organic bridge is sufficiently inefficient, electron transfer may take place instead by direct "through-space" overlap between the surface and the Co(III) acceptor orbitals. The availability of such a pathway has been suggested to explain the relative insensitivity of k_{et} to the presence of additional CH_2 groups in some homogeneous intramolecular systems.[21a] The similar insensitivity observed here (Table I) suggests that the present systems resort to such a nonmediated pathways once the more facile transport route via the organic ligand is sufficiently hindered. It is perhaps surprising that the outer-sphere pathway followed by the acetate complex exhibits a larger value of k_{et} than for the surface-bound nonconjugated complexes given that several of the latter reactants should be sufficiently flexible to allow the Co(III) center to approach closely to the electrode surface. One possibility is that such conformations are relatively unfavorable, yielding smaller effective frequency factors and hence smaller values of k_{et}. However, further speculation is unwarranted in lieu of more definitive structural information.

The relative imprecision and incompleteness of the rate data obtained at gold and copper surfaces preclude such detailed analyses. Nonetheless, significant differences are found in the values of k_{et} measured for each reaction at mercury, gold, and copper electrodes; generally these lie in the sequence Hg $\gtrsim$ Au > Cu. A notable feature at gold is that only small differences in k_{et} are seen between the conjugated- and nonconjugated-bridged reactants. This suggests that a reaction pathway is available at this surface, possibly involving direct surface–Co(III) orbital overlap, where bridging ligand conjugation is no longer especially advantageous. Differences in reactant orientation may be responsible. However, the significantly smaller values of k_{et} at gold and especially copper surfaces are somewhat surprising on this basis. The origin of these substrate effects upon k_{et} may well lie partly in differences in the "surface thermodynamic" contribution ($\ln K_p - \ln K_s$), to ΔG^*_{et} (eq 2). Indeed such differences are not unexpected in view of the extremely strong binding of the thiophene ligands at gold and copper; the strength of coordinate surface bonding is expected to increase in the sequence Hg < Au < Cu.[5] However, quantitative treatments are precluded in the absence of quantitative information on the adsorption thermodynamics at the solid surfaces.

Conclusions

It is apparent that the energetics of organic-bridged electron transfer at metal surfaces can depend significantly on the nature and extent of the electronic coupling between the redox center and the electrode. These interactions are noticeably dependent upon the structure of the organic bridging group and the metal substrate composition as well as upon the nature of the redox center and its immediate environment. In contrast to earlier expectations,[2] the present results indicate that nonadiabaticity, at least for electron transfer through extended organic bridges, may be as common as it appears to be for such processes in homogeneous solution. The outer-sphere electroreduction of $Cr(OH_2)_6^{3+}$ also appears to be marginally nonadiabatic on the basis of rate comparisons with related inner-sphere processes.[32] Further studies of the electron-transfer kinetics of transition-metal reactants bound to metal surfaces using a variety of organic structural units incorporating sulfur as a "sulfur lead-in" group are underway in our laboratory.

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Registry No. I, 55835-99-9; II, 88563-74-0; III, 88563-75-1; IV, 88563-76-2; V, 88642-97-1; VI, 88563-77-3; VII, 88563-78-4; VIII, 88563-79-5; IX, 88563-80-8; $Co^{III}(NH_3)_6L$ (L = 2-furancarboxylic acid), 51965-57-2; $Co^{III}(NH_3)_5L$ (L = 3-furancarboxylic acid), 88563-81-9; $Co^{III}(NH_3)_5L$ (L = 2-(carboxyethenyl)furan), 52021-51-9; $Co^{III}(NH_3)_5(CH_3COO^-)$, 16632-78-3; $Ru(NH_3)_6^{2+}$, 19052-44-9; Hg, 7439-97-6; Au, 7440-57-5; Cu, 7440-50-8.

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(31) Values of δr in this range have recently been estimated for the reduction of structurally similar Cr(III) ammine complexes from a comparison of inner- and outer-sphere reactivities.[32]

(32) Hupp, J. T., Weaver, M. J. *J. Phys. Chem.*, in press.