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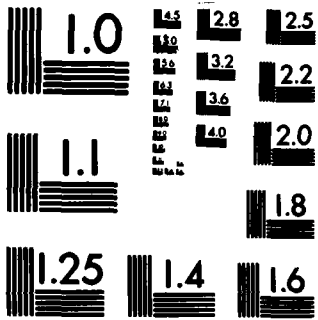
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Dependence of Tunneling Probability upon

Donor-Acceptor Separation Distance

by

T. T-T. Li and M. J. Weaver

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Department of Chemistry

Purdue University

West Lafayette, IN 47907

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INTRAMOLECULAR ELECTRON TRANSFER AT METAL SURFACES. IV. DEPENDENCE  
OF TUNNELING PROBABILITY UPON DONOR-ACCEPTOR SEPARATION DISTANCE.

Tomi T. T. Li and Michael J. Weaver\*  
Department of Chemistry, Purdue University, West Lafayette, IN 47907

There is currently much interest in elucidating the manner in which electron transfer occurs for large separations between the donor and acceptor sites.<sup>1-5</sup> Activity in this area has been heightened recently with the examination of a number of binuclear transition metal and related systems in which the redox centers are separated by a variety of saturated, relatively rigid organic linkages.<sup>1-3</sup> These data indicate that reasonably facile electron transfer can occur over substantial distances (10-20 Å), probably via highly nonadiabatic pathways.

A key question concerns the dependence of the electron-tunneling probability on the donor-acceptor separation distance. We have recently been examining the kinetics of a number of "surface intramolecular" processes, i.e. where one of the redox centers is replaced by a metal surface.<sup>6</sup> Included are surface attachment groups consisting of extended organic bridges.<sup>6c</sup> Here we report measurements on a series of such systems containing saturated surface anchoring groups. The results provide the first direct information on electron tunneling-distance relationships for heterogeneous systems.

Table I contains rate data for the reduction of pentaamminecobalt(III) anchored to gold or mercury surfaces by means of a series of thioalkylcarboxylate ligands. Each ligand contains one or two strongly adsorbing sulfur atoms, being separated from the coordinated carboxylate group by means of a variable length alkyl chain. The synthesis of these complexes followed the general procedures described in ref. 6c. Each reactant is sufficiently strongly adsorbed at gold so to yield a close-packed monolayer (surface concentration,  $\Gamma$ , ca  $1.5$  to  $2 \times 10^{-10}$  moles  $\text{cm}^{-2}$ ) even for very low (10-50  $\mu\text{M}$ ) bulk concentrations. Both rate and adsorption data were

obtained by using rapid linear sweep voltammetry as described in ref. 6c. The rate constants,  $k_{et}^{-300}$  ( $\text{sec}^{-1}$ ), refer to the reduction of surface-attached Co(III) at -300 mV vs saturated calomel electrode (s.c.e.). [Other choices of the common potential yielded essentially the same relative values of  $k_{et}$  since the transfer coefficients,  $\alpha_{et}$  ( $= -(RT/F)(d \ln k_{et}/dE)$ ), are approximately invariant,  $0.58 \pm 0.02$  (Table I).]

Inspection of Table I reveals that the values of  $k_{et}^{-300}$  at gold decrease substantially (ca  $10^4$  fold) as the number,  $n$ , of alkyl carbons increase from one to five. Lengthening the pendant thiol group, however, yielded only minor rate variations. These rate decreases contrast the virtually invariant second-order rate constants,  $k_{Ru}$  ( $M^{-1} \text{sec}^{-1}$ ), observed for the homogeneous outer-sphere reduction of these complexes by  $\text{Ru}(\text{NH}_3)_6^{2+}$  (Table I). The unimolecular reduction of each complex at mercury also yielded approximately constant rates, the values of  $k_{et}^{-300}$  approximating those observed at gold for the shortest alkyl group reactants (Table I).

The tenacious adsorption at gold presumably yields a rigidly packed matrix, constraining the Co(III) redox center to lie progressively further from the metal surface as the number of bridging alkyl carbons increase. The reactant bound to mercury, on the other hand, should be markedly more flexible since submonolayer adsorption ( $\Gamma \sim 5 \times 10^{-11}$  moles  $\text{cm}^{-2}$ ) is involved, presumably enabling Co(III) to closely approach the metal surface in each case. Although there is evidence<sup>8,9</sup> that the values of  $k_{et}$  seen at mercury for these, as for similarly nonconjugated reactants,<sup>6c</sup> reflect moderately nonadiabatic pathways (where the transmission coefficient  $\kappa_{el} \sim 0.05$ <sup>8</sup>), this flexibility therefore appears to provide an alternative "through space" mechanism irrespective of the alkyl chain length (c.f. homogeneous systems<sup>2c</sup>). Consequently, the striking decrease in  $k_{et}$  seen at gold is attributed to the progressively diminution of  $\kappa_{el}$  as the surface - Co(III) separation distance increases. The rigid impervious nature of the adsorbed layers at gold is also evidenced by comparable (up to ca  $10^4$  fold) rate decreases observed for the *outer-sphere* reduction of  $\text{Co}(\text{NH}_3)_5\text{acetate}^{2+}$  upon coating the gold surface with these films.

Figure 1 is a plot of  $\log k_{et}^{-300}$  at gold for the five reactants against the estimated bond distances,  $r$ , between the metal surface and the Co(III) redox centers,<sup>7</sup> (or similarly, against  $n$ ). The approximately linear plot observed is consistent with the relation<sup>10</sup>

$$\kappa_{el}^{r_2} = \kappa_{el}^{r_1} \exp[-\beta(r_2 - r_1)] \quad (1)$$

for a pair of donor-acceptor distances  $r_1$  and  $r_2$ . The slope of the straight line shown in Figure 1 yields  $\beta = 1.45 \text{ \AA}^{-1}$ . This value is very close to that predicted,  $1.4 \text{ \AA}^{-1}$ , for electron tunneling in a medium via a square 2 eV barrier.<sup>11</sup> Comparable values of  $\beta$  have also been obtained from *ab initio* calculations for outer-sphere electron transfer.<sup>5d</sup> A comparable value, ca  $1.3 \text{ \AA}^{-1}$ , is obtained from rate data<sup>2c</sup> for electron tunneling through oligoproline bridging ligands, although the distance dependence of  $k_{et}$  was attributed<sup>2c</sup> partly to changes in the solvent reorganization barrier  $\Delta G_{os}^*$ . This latter factor is less likely to influence the  $k_{et} - r$  dependence for electrochemical reactions since  $\Delta G_{os}^*$  should be almost independent of  $r$  for  $r \geq 6 \text{ \AA}$ .<sup>12</sup>

The present data can also be utilized to roughly estimate *absolute* values of  $\kappa_{el}$ , assuming that the observed rates at mercury,  $k_{et}^{-300} \approx 5 \times 10^3 \text{ sec}^{-1}$ , correspond to  $\kappa_{el} \sim 0.05$  (*vide supra*). From this we deduce that  $\kappa_{el} \sim 2 \times 10^{-5}$  for  $n = 5$  at gold, for which  $r \sim 15 \text{ \AA}$  (Fig. 1) [c.f. ref. 1]. Of course, the actual surface - Co(III) distances may be shorter than the estimates in Fig. 1 if the carbon linkages are somewhat staggered. Assuming  $120^\circ$  bond angles diminishes the effective  $r$  values about 15%. Even though a distribution in the surface-Co(III) distances will result from variations in the film structure, the measured  $k_{et}$  values will tend to reflect the smaller distances since  $k_{et}$  increases with decreasing  $r$ .

The present results are compatible with our recent deduction for some related *outer-sphere* electrochemical reactions that  $\kappa_{el} < 1$  for  $r \geq 6 \text{ \AA}$ ,<sup>13</sup> (c.f. homogeneous reactions<sup>5d</sup>). These results apparently refute the claim<sup>14</sup>

that heterogeneous electron transfer will be adiabatic even at large (10-20 Å) separations due to the continuum of electronic states at metal surfaces. Rather they reveal striking behavioral similarities for electron tunneling in heterogeneous and homogeneous environments.

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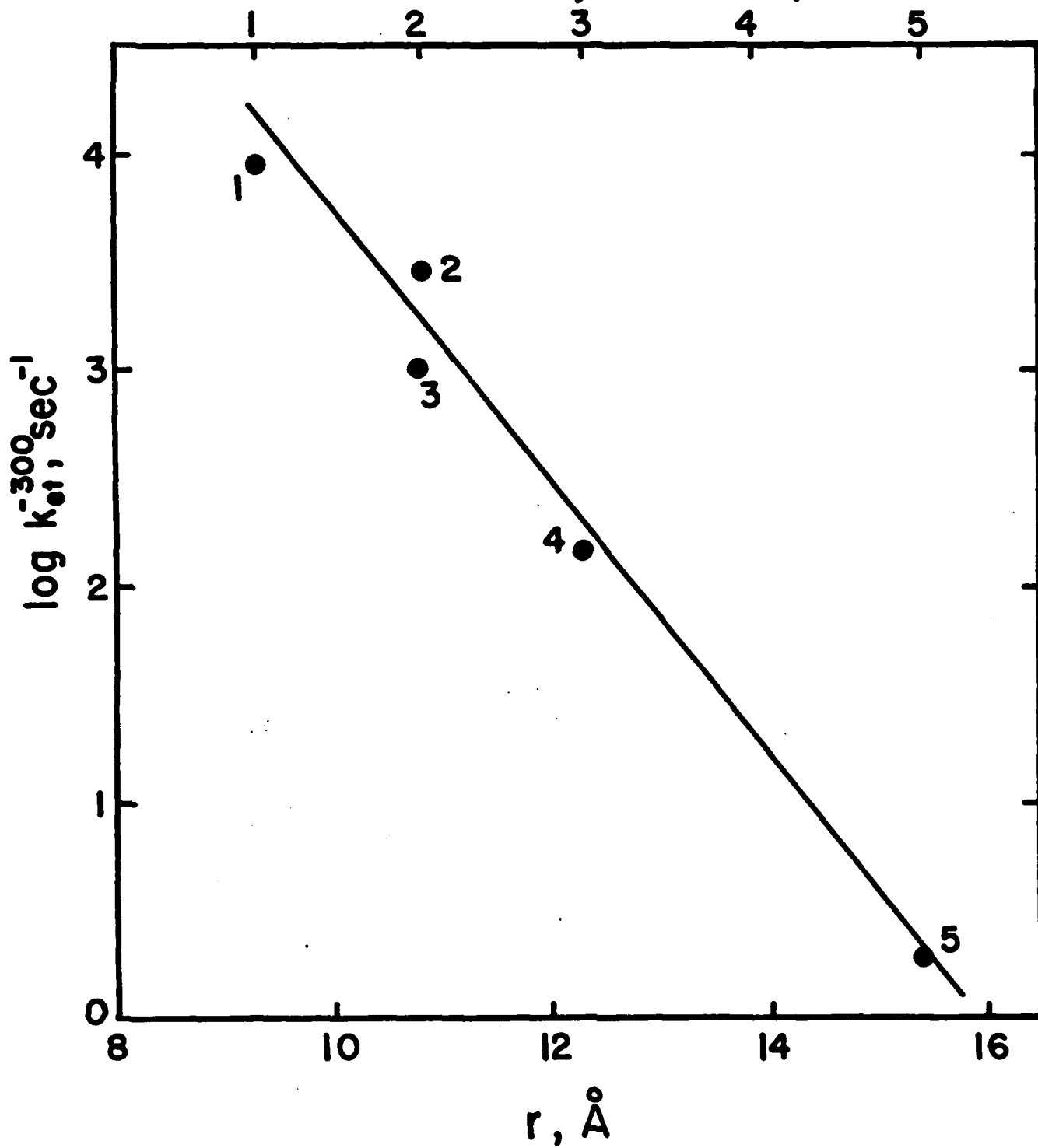
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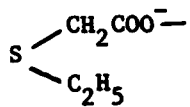
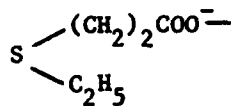
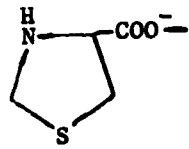
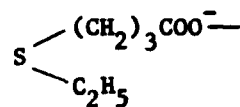
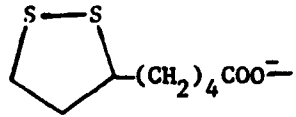
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7. Bond distances: C-C, 1.54 Å; C-O, 1.36 Å; O-Co(III), 2.3 Å; C-S, 1.8 Å; S-Au, ca 2.3 Å; values from A. J. Gordon, R. A. Ford (eds.), "The Chemist's Companion", Wiley, N.Y.; 1972, p. 108.
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Number of alkyl carbons, n



**TABLE I.** Rate data for Reduction of  $\text{Co}^{\text{III}}(\text{NH}_3)_5\text{X}$  with Surface-Attaching Ligands X.

X	Surface	$k_{\text{et}}^{-300}$ <sup>a</sup> sec <sup>-1</sup>	$\alpha_{\text{et}}$ <sup>b</sup>	$k_{\text{Ru}}$ <sup>c</sup> <u>M</u> <sup>-1</sup> sec <sup>-1</sup>
(1) 	Au	$9.5 \times 10^3$	0.57	0.022
	Hg	$4.5 \times 10^3$	0.56	
(2) 	Au	$3.0 \times 10^3$	0.61	0.025
	Hg	$4.0 \times 10^3$	0.60	
(3) 	Au	$1.0 \times 10^3$	0.60	0.023
	Hg	$5.5 \times 10^3$	0.80	
(4) 	Au	$1.4 \times 10^2$	0.60	0.024
	Hg	$3.0 \times 10^3$	0.60	
(5) 	Au	2.0	0.60	0.016
	Hg	$5.5 \times 10^3$	0.62	

<sup>a</sup>Unimolecular rate constant for reduction of surface-attached complex in 0.1 M  $\text{NaClO}_4$  + 5 mM  $\text{HClO}_4$  at -300 mV vs s.c.e., determined by using rapid linear sweep voltammetry as described in ref. 6c.

<sup>b</sup>Transfer coefficient of electron-transfer step, from  $\alpha_{\text{et}} = -(RT/F)(d \ln k_{\text{et}}/dE)$ .

<sup>c</sup>Second-order rate constant for homogeneous reduction of  $\text{Co}(\text{III})$  complex by  $\text{Ru}(\text{NH}_3)_6^{2+}$  in 0.05 M sodium trifluoroacetate-trifluoroacetic acid, evaluated as described in ref. 6c.

Figure Caption

Plot of unimolecular rate constants for electroreduction of surface-attached  $\text{Co}^{\text{III}}(\text{NH}_3)_5\text{X}$  complexes at gold electrodes at  $-300 \text{ mV}$ ,  $k_{\text{et}}^{-300}$ , versus the estimated through-bond surface - Co(III) distance,  $r$ , and number of alkyl carbons,  $n$ .

Data from Table I; identifying numbers as listed in Table I.

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ABSTRACT

Unimolecular electron-transfer rate constants,  $k_{et}$ , are reported for the one-electron reduction of pentaamminecobalt(III) attached to gold and mercury electrodes via thioalkylcarboxylate ligands containing varying numbers, n, of alkyl carbons. While similar values of  $k_{et}$  were found at mercury for each reaction, for close-packed monolayers at gold the  $k_{et}$  values decreased by circa  $10^{-4}$  to the 4th power as n increased from one to five. This effect is identified with increasingly nonadiabatic pathways as n increases, a linear plot of  $\log(k_{et})$  versus n being obtained. The results provide estimates of the electronic transmission coefficient as a function of the surface-Co(III) separation distance.

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