

Scanning Electrochemical Microscopy with Gold Nanotips: The Effect of Electrode Material on Electron Transfer Rates

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The disk-type, polished Au nanoelectrodes were prepared, characterized, and used as tips in the scanning electrochemical microscope (SECM). Kinetic parameters were measured for several rapid heterogeneous electron transfer (ET) reactions and compared to those obtained previously at Pt nanoelectrodes. The kinetics of most investigated ET processes were found to be independent of the electrode material. In contrast to the previously reported results, the rate constant of hexaammineruthenium(III) reduction was somewhat higher at Pt than at Au electrodes in different electrolyte solutions. This finding suggests that this reaction exhibits some degree of nonadiabaticity.

Introduction

The availability of nanometer-sized electrochemical probes with well-characterized geometry and desired properties is essential for electrochemical experiments on the nanoscale.¹ The nanoelectrodes of various geometries, such as, disks, bands, cones, and recessed electrodes, were produced by several research groups.^{2–15} We reported recently the preparation and characterization of the disk-type, polished nanoelectrodes with a radius of $a \geq 4$ nm.^{15a} A small RG value (i.e., the ratio of the insulating sheath radius to a) of ≤ 10 allowed such electrodes to be used as tips in scanning electrochemical microscopy (SECM) and to serve as nanoprobe for experiments inside living cells^{15c} and in electrochemical nanojunctions.^{15d}

All nanoelectrodes previously fabricated in our laboratory were made of Pt. Other metal (e.g., Au) electrodes may be required for various applications (e.g., surface modification by molecular self-assembly,¹⁶ electrocatalysis,¹⁷ or kinetic measurements). Zhang et al.^{3d} recently reported the preparation of nanometer-sized Au and Pt glass-sealed nanoelectrodes. In that work, the same methodology was used to fabricate Pt and Au nanoelectrodes with thick insulating glass (large RG). However, significant modifications in pulling procedures are required to produce Au SECM nanotips with $RG \leq 10$.

In this article, we employ Au nanoelectrodes to study heterogeneous electron transfer (ET) kinetics. With nanoelectrodes, one can attain a high rate of mass transport and study kinetics of fast ET under steady-state conditions.¹⁸ In the previous study,^{15a} the kinetic parameters of several rapid ET reactions were extracted from SECM voltammograms obtained at the tip electrode positioned near a conductive substrate. The tip potential was swept slowly to obtain a steady-state voltammogram, while the substrate was poised at a constant potential, at which the regeneration of the redox mediator was diffusion controlled.¹⁹ In feedback-mode SECM experiments, the shorter the separation distance between the tip and the conductive substrate (d), the larger the mass-transfer coefficient (m).²⁰ Thus, the mass-transfer rate could be changed within a wide range

(e.g., by more than 2 orders of magnitude^{15a}) by varying a and d . Using this approach, the kinetic parameters were measured for four rapid outersphere ET reactions (i.e., the oxidations of ferrocenemethanol in water and of ferrocene in acetonitrile, and the reductions of $\text{Ru}(\text{NH}_3)_6^{3+}$ in 0.5 M KCl and of TCNQ in acetonitrile) at Pt nanoelectrodes.^{15a} The standard rate constants (k°) measured at nanoelectrodes were similar to or somewhat higher than the values obtained previously at larger electrodes. They also were essentially independent of both from a and d – an important test of the data validity.

No direct correlation was found in ref 15a between the measured electrochemical rate constants and corresponding self-exchange rate constants (k_{ex}): the lowest k° was measured for the redox couple with the fastest k_{ex} (TCNQ/TCNQ^{•−}), and vice versa, the fastest heterogeneous rate constant was obtained for $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ in 0.5 M KCl, whose k_{ex} was the lowest among the studied couples. It was suggested that the measured rates may reflect the differences in adiabaticity of those heterogeneous ET processes. Although it is pretty common to invoke the adiabaticity argument when the measured ET rates are lower than those predicted theoretically, few experimental observations of definitely nonadiabatic electrochemical ET have been reported to date.²¹

The extent of adiabaticity can be evaluated by probing the effect of the electrode material on the ET rate. According to Gosavi and Marcus,²² the rate constant is expected to be proportional to the density of electronic states of the metal at the Fermi level (ρ_{F}) for nonadiabatic ET and independent of ρ_{F} in the adiabatic case. For the former case, they predicted the ratio of standard rate constants of the same ET at Pt and Au electrodes to be ~ 1.8 (assuming that the reorganization energy, λ , is the same for both electrodes) because the ρ_{F} of Pt is larger. Whereas this prediction has been corroborated experimentally for ET across self-assembled monolayers,²³ no similar results have yet been obtained at bare metal electrodes. Similar rate constants were measured at Pt and Au for various redox species, for example, benzoquinone in dimethylformamide,²⁴ or $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ in 1 M KF.²⁵ In addition to double-layer effects that can compromise the comparative ET measurements,²³ relatively low mass-transfer rates attainable at macroelectrodes may have thwarted previous attempts to detect differences in k° at different metal surfaces. Here, we compare the results of

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kinetic experiments at Au nanoelectrodes to those done at similarly sized Pt tips in ref 15a to investigate the effect of electrode material on the rates of fast ET reactions and detect possible nonadiabaticity.

Experimental Section

Chemicals. Ferrocenemethanol (FcCH_2OH , 97%) from Aldrich (Milwaukee, WI) was recrystallized twice from acetone. Hexaammineruthenium(III) chloride (99%) was obtained from Strem Chemicals (Newburyport, MA). Tetrathiafulvalene (97%), 2,2,6,6-tetramethyl-1-piperidinyloxy free radical (TEMPO, 96%) and methylphenothiazine (98%) were from Aldrich (Milwaukee, WI). 7,7,8,8-tetracyanoquinodimethane (TCNQ, 98%) and ferrocenemethanol (FcCH_2OH , 97%) from Aldrich were recrystallized twice from acetone. Ferrocene (Fc, 98%; Aldrich) was sublimed twice before use. Tetrabutylammonium perchlorate (Fluka), NaCl, KF, KNO_3 , and KCl (99+%, Aldrich) were used as supporting electrolytes. Aqueous solutions were prepared from deionized water (Milli-Q, Millipore Co.). Either 99.95% acetonitrile (Aldrich) or twice distilled HPLC grade DCE (Sigma-Aldrich) was used to prepare organic solutions.

Electrodes and Electrochemical Cells. Polished Au working electrodes (~ 40 to ~ 200 nm radius) were prepared and characterized as described below. A two-electrode configuration was employed with a 0.25 mm diameter Ag wire coated with AgCl serving as a reference electrode. All potential values below are reported versus this reference. Evaporated Au films (100 nm thick) on glass prepared with the aminosilane coupler and annealed²⁶ were obtained as a gift from Alexander Vaskevich (Weizmann Institute of Science) and used as a conductive SECM substrate. The cell was made by attaching a 7 mm glass tube to the Au coated slide, which was mounted on a vibration-isolated horizontal stage. In the negative feedback mode, a bare glass slide was used as an insulating substrate to check the tip geometry.

The fabrication of a nanotip starts with pulling a micrometer-sized Au wire into a glass capillary, as described previously.^{15a} Briefly, an annealed 25 μm wire (Goodfellow) was inserted into a borosilicate capillary (1.0 mm o.d., 0.2 mm i.d.), which was fixed in the V groove of the Sutter P-2000/G laser pipet puller. The programs designed to produce Au nanoelectrodes with a desired size and shape were different from those used previously to pull Pt electrodes because of the comparatively low melting point of gold. For example, the parameter heat that controls the output power of a laser was set somewhat lower for gold (400) than for platinum (500), and the velocity parameter value was kept higher for Au (30) than for Pt (15). The larger value of the latter parameter resulted in a lower temperature of the Au wire at the moment when the capillary was pulled.

A pulled capillary with a sealed Au wire was polished using a BV-10 micropipet beveller (Sutter) under video microscopic control. A micromanipulator was used to move the capillary vertically toward the rotating disk to which a 50 nm lapping tape (Precision Surfaces International, Houston, TX) was attached. During polishing, the pipet axis was made exactly perpendicular to the rotating disk using a plumb bob and a two-axis bubble level. (See ref 15b for details of the tip/polisher and tip/substrate alignment.) Additional fine polishing was done with 50 nm alumina particles placed on the same rotating disk. The polished electrodes were rinsed with water and annealed in the oven at 90 $^\circ\text{C}$ for an hour.

For kinetic measurements by SECM, it is essential to bring the tip very close to the substrate surface. The minimum attainable tip/substrate separation distance should be $\sim 0.1 a$ or

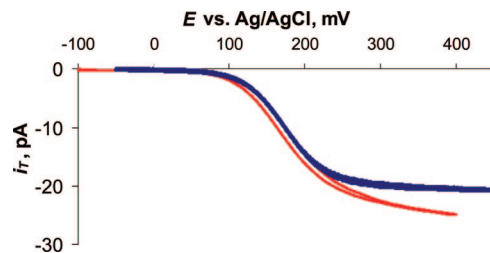


Figure 1. Steady-state voltammograms of 1 mM FcCH_2OH before (red) and after (blue) the 70 nm radius Au tip was polished by stirring an aqueous suspension of 50 nm alumina particles. The potential sweep rate was 50 mV/s.

smaller. This can be done only if the metal core of the tip is not recessed into the insulating glass and the RG is sufficiently small. Unfortunately, repolishing the tip, which may be required to clean it and ensure reproducibility of the results, increases the thickness of the glass sheath and may result in a slight recess of the Au surface. This problem can be avoided by using an aqueous suspension of alumina particles to repolish the tip. The polishing was done by moving the tip inside a concentrated suspension (very soft paste) of 50 nm alumina particles in water. Figure 1 shows two voltammograms of 1 mM of FcCH_2OH at a 70 nm radius Au tip before (red) and after (blue) repolishing it in a suspension of 50 nm alumina. A marked improvement in the electrode response is not surprising if one keeps in mind that the tip radius was comparable to that of an average alumina particle. Random collisions of particles with the tip result in gentle and efficient polishing.

Instrumentation and Procedures. A home-built SECM instrument and experimental procedures were described previously.^{15a,b} Briefly, the initial approach of the nanotip to the substrate surface was attained using a z axis Inchworm motor (EXFO-Burleigh) to move the tip toward the substrate at a relatively slow speed (e.g., 200 nm/s). The motion was stopped instantly when the change in tip current was detected, that is at the tip/substrate separation distance equivalent to several tip radii. The final approach was done using a piezo actuator (PI-841, Physik Instrumente, Germany) to move the tip toward the substrate at a very low speed (5 to 30 nm/s) and recording the tip current as a function of separation distance. The approach was monitored by a video microscope. A proper tip/substrate alignment was achieved as described in ref 15b.

To obtain an approach curve, the tip was biased at a potential where the oxidation (or reduction) of the mediator species occurred at a diffusion-controlled rate; the mediator regeneration at the unbiased Au substrate was also diffusion-controlled. For SECM voltammetric experiments, the nanotip was positioned at a suitable distance from the substrate, and its potential was scanned. The corresponding approach curve was used as a distance calibration to determine the tip/substrate distance from the diffusion limiting current. All experiments were carried out at room temperature (23 ± 2 $^\circ\text{C}$) inside a Faraday cage. Steady-state voltammograms were obtained using an EI-400 bipotentiostat (Ensmann Instruments, Bloomington, IN) or a BAS 100B electrochemical workstation (Bioanalytical Systems, West Lafayette, IN). The solution containing $\text{Ru}(\text{NH}_3)_6^{3+}$ was purged with high-purity nitrogen for at least 30 min before voltammetric measurements.

Results and Discussion

Electrode Characterization. Cyclic voltammetry and SECM were used to check that the surface of a polished gold

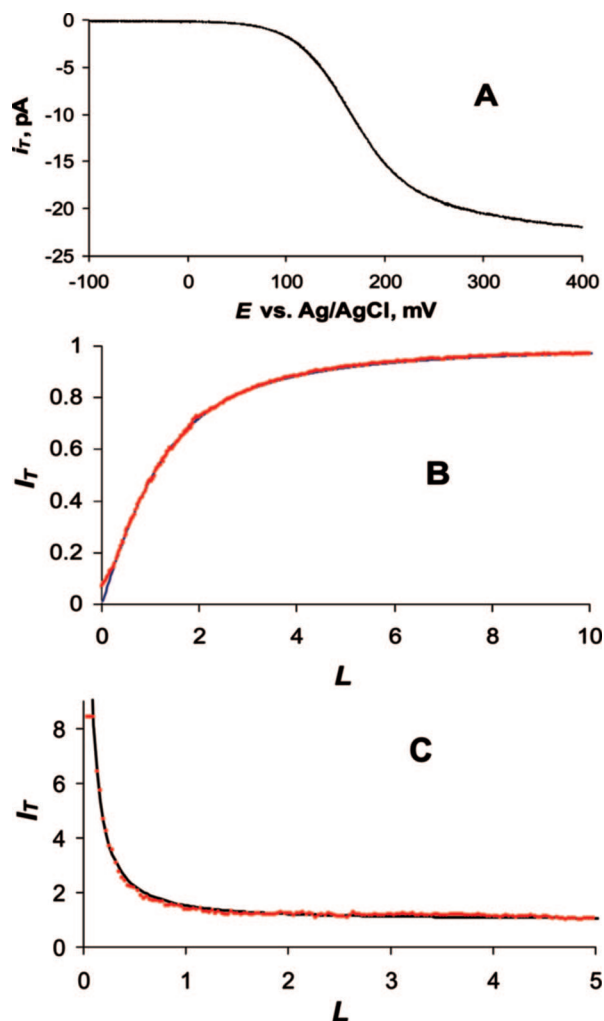


Figure 2. Steady-state voltammogram (A) and SECM approach curves (B) and (C) obtained at a Au tip in solution containing 1 mM FcCH₂OH and 0.2 M KNO₃. $a = 68$ nm (A) and (B), and 60 nm (C). Theoretical curves (solid lines) were calculated with $RG = 10$ for negative feedback (B) and diffusion-controlled positive feedback (C);²⁷ symbols are experimental data. The current is normalized by the value measured in the bulk solution. The tip approached the substrate with a 5 nm/s (B) and 10 nm/s (C) speed. The potential sweep rate was $\nu = 50$ mV/s (A).

nano-electrode is flat and not recessed. A steady-state voltammogram of 1 mM ferrocenemethanol (part A of Figure 2) is fully retraceable and well shaped with a flat diffusion plateau. The tip radius, $a = 68$ nm was obtained from eq 1

$$i_{T,\infty} = 4FDac^* \quad (1)$$

where F is the Faraday constant, $D = 7.8 \times 10^{-6}$ cm²/s is the diffusion coefficient of FcCH₂OH,^{15a} and c^* is its concentration in solution. An SECM current versus distance curve obtained with the same Au tip approaching an insulating substrate (part B of Figure 2, symbols) was fitted to the theory for negative feedback (solid line)²⁷ using the same radius value. The RG value ($RG = 10$) was determined from the same current–distance curve, as discussed previously.^{15a,27} A high positive feedback current obtained with a 60 nm Au tip approaching a conductive substrate (part C of Figure 2) is indicative of a flat, nonrecessed, and well-polished tip surface. $RG = 10$ obtained from parts B and C of Figure 2 is typical of the Au tips used in this work. Although a very careful tip/substrate alignment (Experimental Section) was required to attain short separation distances with

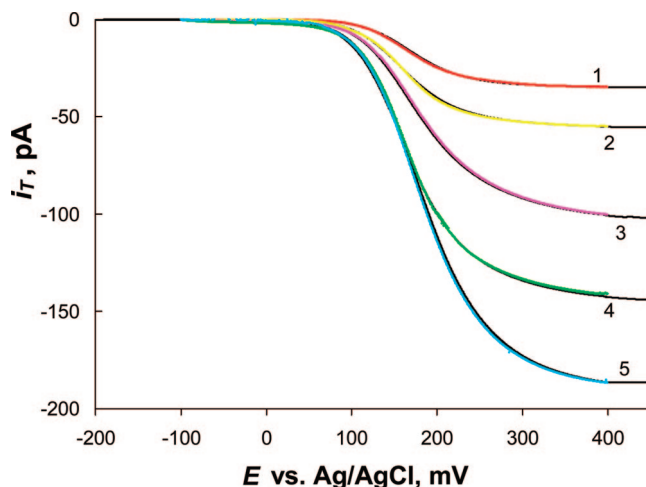


Figure 3. Experimental steady-state voltammograms of 1 mM FcCH₂OH obtained at different separation distances between the 109 nm Au tip and the Au substrate. $d = \infty$ (1), 72 nm (2), 35 nm (3), 31 nm (4), and 21 nm (5); $\nu = 50$ mV/s.

a relatively large RG , we preferred to employ such tips for measurements of fast heterogeneous kinetics because the theory (eq 2) was developed for $RG = 10$.^{15a}

Kinetics of ET Reactions at Au Nanoelectrodes. Kinetic parameters of FcCH₂OH oxidation in 0.2 M NaCl (6.8 ± 0.7 cm/s, $\alpha = 0.42 \pm 0.03$) were extracted in ref 15a from a number of voltammograms obtained at Pt nanoelectrodes of different radii (from 25 to 290 nm). Figure 3 shows a family of voltammograms of the same ET reaction obtained with a 109 nm Au tip positioned at different distances from the conductive, Au film substrate. k° and the transfer coefficient (α) were obtained by fitting the voltammograms to eq 2:^{15a}

$$I_T(E, L) = \frac{0.78377}{L(\theta + 1/\kappa)} + \frac{0.68 + 0.3315 \exp(-1.0672/L)}{\theta \left[1 + \frac{\pi}{\kappa} \frac{2\kappa\theta + 3\pi}{4\kappa\theta + 3\pi^2} \right]} \quad (2)$$

where $L = d/a$, E is the tip potential, $\kappa = \pi\lambda \exp[-\alpha F(E - E^\circ)/RT]/(4F_i)$, $\lambda = k^\circ a/D$, $\theta = 1 + \exp[F(E - E^\circ)/RT]D_O/D_R$, E° is the formal potential, R is the gas constant, T is the temperature, D_O and D_R are the diffusion coefficients of oxidized and reduced forms of redox species ($D_O = D_R = D$ is assumed below), and F_i is the normalized diffusion limiting tip current for the same L at a conductive substrate:

$$I_T^c = 0.68 + 0.78377/L + 0.3315 \exp(-1.0672/L) \quad (3)$$

The tip current $I_T(E, L)$ in eq 2 is normalized by the steady-state diffusion limiting current to a microdisk electrode, $i_{T,\infty}$, which is given by eq 1 for a sufficiently large RG (e.g., ~ 10).

Kinetic parameters extracted from the series of SECM voltammograms obtained at five different Au tips are summarized in Table 1. As discussed previously,^{15a,19} the upper limit for the measurable standard rate constant can be given in terms of the dimensionless kinetic parameter $\lambda' = k^\circ d/D = Lk^\circ a/D$. The tip voltammogram is essentially reversible if $\lambda' \gtrsim 10$. When the tip is far from the substrate, the condition of reversibility is $\lambda = k^\circ a/D \gtrsim 10$. Thus, the kinetic parameters in Table 1 were obtained only from voltammograms that yielded $\lambda' < 10$ (or $\lambda < 10$ at $L \gg 1$). Similar to the results obtained previously at Pt nanoelectrodes, there is no apparent correlation between the determined kinetic parameters and a or d values. Essentially the same formal potential value (within ± 5 mV) was found from

TABLE 1: Kinetic Parameters of FcCH₂OH Oxidation at Au Nanoelectrodes in 0.2 M NaCl

<i>a</i> , nm ^a	<i>L</i>	<i>k</i> ^o , cm/s	α	<i>E</i> ^{o'}	λ' or λ
153	∞		reversible		
153	0.86		reversible		
153	0.42	9.0	0.31	153	7.4
153	0.34	10.5	0.30	151	7.0
153	0.21	9.8	0.30	142	4.0
109	∞		reversible		
109	0.66	7.3	0.32	172	6.8
109	0.32	5.5	0.33	168	2.5
109	0.28	8.9	0.32	161	3.5
109	0.19	8.3	0.41	162	2.3
65	∞	5.3	0.57	131	4.5
65	0.6	6.8	0.51	121	3.5
57	∞	6.7	0.51	192	4.8
57	1.5	7.5	0.49	196	8.2
57	0.71	7.8	0.49	190	4.0
55	∞	8.2	0.45	138	6.3
55	2.15	9.1	0.57	134	5.2
55	1.2	11.6	0.48	135	5.9

^a Calculated from eq 1 with $D = 7.8 \times 10^{-6}$ cm²/s.^{15a}**TABLE 2: Kinetic Parameters of Ru(NH₃)₆³⁺ Reduction at Au Nanoelectrodes (Solution Contained 2 mM Ru(NH₃)₆³⁺ and 0.5 M KCl)**

<i>a</i> , nm ^a	<i>L</i>	<i>k</i> ^o , cm/s	α	<i>E</i> ^{o'}	λ'
134	∞		reversible		
134	0.62		reversible		
134	0.53		reversible		
134	0.40	10.5	0.3	151	8.4
134	0.36	11.4	0.30	142	8.2
98	∞		reversible		
98	0.31	13.3	0.51	131	6.0
98	0.25	15.0	0.51	133	5.4
98	0.18	18.4	0.49	127	4.9
84	∞		reversible		
84	0.26	19.8	0.63	162	6.5
84	0.20	12.5	0.67	156	7.1
62	∞		reversible		
62	0.87	9.1	0.35	134	8.0
62	0.67	11.6	0.33	135	5.0

^a Calculated from eq 1 with $D = 6.7 \times 10^{-6}$ cm²/s.^{15a}

different voltammograms obtained at the same tip. The variations between *E*^{o'} values obtained with different tips are due to the slow shift in the coated-wire reference potential (on the time scale of several days). The mean values of the kinetic parameters from Table 1 are $k^o = 8 \pm 1$ cm/s and $\alpha = 0.42 \pm 0.06$. (Here and below, the uncertainties are 95% confidence intervals.) The determined α value is the same as the one found for FcCH₂OH oxidation at Pt nanoelectrodes, and the k^o value is slightly higher than the one in ref 15a (6.8 ± 0.7 cm/s). This difference is within the range of our experimental uncertainty, and a slightly larger rate constant measured at Au electrodes indicates that a higher density of electronic states in Pt is not a factor here. No statistically significant difference was also found between kinetic parameters of the oxidation of Fc in acetonitrile measured at 10 Au nanoelectrodes ($k^o = 8.0 \pm 0.5$ cm/s, $\alpha = 0.44 \pm 0.03$) and those obtained previously^{15a} at Pt tips ($k^o = 8.4 \pm 0.2$ cm/s, $\alpha = 0.47 \pm 0.02$). These findings indicate that the oxidations of FcCH₂OH in water and Fc in acetonitrile are adiabatic processes.²²

A similar approach was used to measure kinetic parameters of the reduction of Ru(NH₃)₆³⁺ in 0.5 M KCl (Table 2). Like it was found above for FcCH₂OH, the mean transfer coefficient value for Ru(NH₃)₆³⁺ reduction at Au electrodes ($\alpha = 0.45 \pm$

TABLE 3: Kinetic Parameters of the Reduction of 2 mM Ru(NH₃)₆³⁺ at Pt and Au Nanoelectrodes in 1 M KF

electrode	<i>a</i> , nm ^a	<i>L</i>	<i>k</i> ^o , cm/s	α	<i>E</i> ^{o'}	λ' or λ
Au	70	∞		reversible		
Au	70	1.1		reversible		
Au	70	0.61	9.3	0.34	−282	6.1
Au	70	0.42	9.1	0.38	−284	4.1
Au	70	0.30	9.6	0.40	−280	3.1
Au	56	∞	9.5	0.48	−282	8.2
Au	56	0.98	10.2	0.46	−278	8.6
Au	56	0.58	9.0	0.38	−276	4.5
Au	56	0.45	9.8	0.42	−278	3.8
Au	56	0.36	8.4	0.46	−280	2.6
Pt	77	∞		reversible		
Pt	77	0.98		reversible		
Pt	77	0.58	11.8	0.37	−272	8.1
Pt	77	0.40	11.4	0.38	−268	5.4
Pt	77	0.21	12.9	0.37	−274	3.2
Pt	62	∞		reversible		
Pt	62	0.78	11.6	0.52	−268	8.6
Pt	62	0.56	11.2	0.38	−258	6.0
Pt	62	0.30	12.6	0.37	−259	3.6

^a Calculated from eq 1 with $D = 6.5 \times 10^{-6}$ cm²/s, which was obtained by steady-state voltammetry at micrometer-size electrodes.

0.09) is exactly the same as that at Pt.^{15a} However, the mean rate constant value at Au surfaces ($k^o = 13.5 \pm 2$ cm/s) is lower than that measured at Pt tips in ref 15a (17.0 ± 0.9 cm/s). The difference between these two mean values is statistically significant: using a *t* test²⁸ at the 95% confidence level, one can find $t_{\text{calcd}} = 3.65$, which is larger than $t_{\text{table}} = 2.1$. The dependence of the rate of Ru(NH₃)₆³⁺ reduction on the nature of the metal surface points to some degree of nonadiabaticity; however, the ratio, $k^o_{\text{Pt}}/k^o_{\text{Au}} = 1.26$ is smaller than the 1.8 value expected for a completely nonadiabatic reaction.

The above finding is different from the results of Iwasita et al.,²⁵ who measured very similar rate constant values for the Ru(NH₃)₆^{3+/2+} couple at different metallic electrodes and concluded that the ET reaction is fully adiabatic. However, the supporting electrolyte in ref 25 was 1 M KF. It was also suggested that the kinetics of Ru(NH₃)₆³⁺ reduction strongly depends on the nature of the supporting electrolyte, and the k^o value greatly increases in the presence of a high concentration of chloride.⁵ Therefore, we determined the kinetics of this reaction at both Pt and Au nanoelectrodes in 1 M KF. The results presented in Table 3 can be summarized as follows: $k^o = 11.9 \pm 0.5$ cm/s, $\alpha = 0.40 \pm 0.05$ (at Pt), and $k^o = 9.3 \pm 0.4$ cm/s, $\alpha = 0.42 \pm 0.03$ (at Au). Similar to the results obtained in KCl, there is no significant difference between the transfer coefficient values measured at Au and Pt electrodes. For both Au and Pt, the mean k^o measured in KF is somewhat (~30%) lower than the corresponding values in KCl. Moreover, in KF the $k^o_{\text{Pt}}/k^o_{\text{Au}}$ ratio is 1.27, that is very close to the 1.26 value obtained in KCl. In either solution, the reduction of Ru(NH₃)₆³⁺ is not completely adiabatic. The discrepancy between this finding and the previously reported results²⁵ is probably due to a very high k^o value, which was hard to accurately measure at macroscopic electrodes back in 1985.

One should notice that the self-exchange rate constant measured for Ru(NH₃)₆^{3+/2+} is significantly (~3 orders of magnitude) lower than that obtained for the ferrocene couple.^{29,30} This data and a higher degree of adiabaticity of FcCH₂OH oxidation discussed above are at variance with the larger k^o values measured for Ru(NH₃)₆³⁺ reduction at both Pt and Au electrodes. A plausible explanation is that the k^o of Ru(NH₃)₆³⁺ reduction is enhanced by the diffuse doublelayer effect (Frumkin

TABLE 4: Kinetic Parameters of the Oxidation of Tetrathiafulvalene in 1,2-Dichloroethane at Pt and Au Nanoelectrodes (Solution Contained 2 mM Tetrathiafulvalene and 0.1 M Tetrabutylammonium Perchlorate)

electrode	<i>a</i> , nm ^a	<i>L</i>	<i>k</i> ^o , cm/s	α	<i>E</i> ^{o'}	λ' or λ
Pt	72	∞	8.6	0.38	352	7.2
Pt	72	0.46	8.8	0.34	354	3.4
Pt	72	0.25	9.1	0.42	354	1.9
Pt	72	0.17	8.4	0.38	350	1.2
Pt	65	∞	8.2	0.41	360	6.2
Pt	65	0.78	8.7	0.35	358	5.1
Pt	65	0.44	8.4	0.36	360	2.8
Pt	65	0.28	9.9	0.35	360	2.1
Au	68	∞	9.4	0.36	348	7.4
Au	68	0.82	8.0	0.41	348	5.2
Au	68	0.45	8.7	0.38	346	3.1
Au	68	0.25	8.6	0.38	345	1.7
Au	54	∞	9.9	0.38	350	6.2
Au	54	0.9	9.7	0.38	352	5.5
Au	54	0.68	8.2	0.36	350	3.5
Au	54	0.32	9.0	0.40	349	1.8
Au	43	∞	8.6	0.45	364	4.3
Au	43	0.87	9.4	0.41	358	4.1
Au	43	0.55	9.1	0.45	352	2.5

^a Calculated from eq 1 with $D = 8.7 \times 10^{-6}$ cm²/s, which was obtained by steady-state voltammetry at micrometer-size electrodes.

correction), which can be expressed as $k_t = k^o \exp((z - \alpha)F\varphi_2/RT)$, where z is the ionic charge and φ_2 is the potential at the outer Helmholtz plane.³¹ Although it is hard to quantitatively evaluate φ_2 and the magnitude of the Frumkin correction at solid nanoelectrodes; this correction should be larger for Ru(NH₃)₆³⁺ ($z = 3$) than for a neutral FcCH₂OH species. Moreover, Ru(NH₃)₆^{3+/2+} is the only redox couple for which the rate constant measured either at Au or at Pt nanoelectrodes was significantly higher than the values obtained previously at macroscopic electrodes. This observation agrees with the theoretical prediction that a double-layer effect on heterogeneous kinetics may be stronger at nanoelectrodes³² (and nanoparticles³³) than at macroscopic electrodes, especially for multi-charged ions.³⁴

Other ET Reactions. The kinetics of several other fast outer-sphere redox couples at Au and Pt nanoelectrodes were investigated. A few of them exhibited near-ideal voltammetric responses at both types of nanoelectrodes. A typical example is the rapid oxidation of tetrathiafulvalene in 1,2-dichloroethane, whose kinetic parameters are essentially the same at Pt ($k^o = 8.8 \pm 0.4$ cm/s, $\alpha = 0.375 \pm 0.02$) and Au ($k^o = 9.0 \pm 0.4$ cm/s, $\alpha = 0.395 \pm 0.02$) surfaces (Table 4). Similar results were obtained for two other redox species, that is TEMPO in acetonitrile and methylphenothiazine in 1,2-dichloroethane (data not shown).

Another group of ET reactions appear to be strongly surface-dependent. A typical example is the reduction of 7,7,8,8-tetracyanoquinodimethane (TCNQ) in acetonitrile. At Pt nanoelectrodes, this process yielded essentially ideal voltammetric responses, and the determined $k^o = 1.1 \pm 0.04$ cm/s^{15a} was relatively slow in contrast to the very fast self-exchange rate constant of TCNQ (4×10^9 M⁻¹s⁻¹³⁵). One could expect this ET to be nonadiabatic and to show significant differences between the rates measured at Pt and Au. However, the voltammograms of TCNQ at Au nanoelectrodes were poorly shaped, and no quantitative kinetic analysis was possible. Similarly, we were unable to obtain well shaped voltammograms at Au nanoelectrodes for Ru(bpy)₃^{3+/2+}, Fe(CN)₆^{3-/4-}, and Fe^{3+/2+} couples.

Conclusions

The flat, polished Au nanoelectrodes were prepared and characterized by SECM and voltammetry. These probes were used to measure the kinetic parameters of several rapid heterogeneous ET reactions by steady-state SECM voltammetry. While the mass transfer rate was changed by varying the tip radius and the tip/substrate separation distance, the determined kinetic parameters were essentially independent of both a and d . For several species including Fc, FcCH₂OH, and tetrathiafulvalene, the standard rate constants and transfer coefficient values measured at Au tips were very similar to those obtained at Pt nanoelectrodes, as expected for adiabatic ET reactions.²² However, the standard rate constants of Ru(NH₃)₆³⁺ reduction in KCl and KF solutions at Au electrodes were found to be lower than those obtained at Pt electrodes, indicating that this reaction is not fully adiabatic.

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