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ARTICLE *in* ANALYTICAL CHEMISTRY · SEPTEMBER 1999

Impact Factor: 5.64 · DOI: 10.1021/ac990399d

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Control of Catechol and Hydroquinone Electron-Transfer Kinetics on Native and Modified Glassy Carbon Electrodes

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The electrochemical oxidation of dopamine, 4-methylcatechol, dihydroxyphenylacetic acid, dihydroxyphenyl ethylene glycol, and hydroquinone was examined on several native and modified glassy carbon (GC) surfaces. Treatment of polished GC with pyridine yielded small ΔE_p values for cyclic voltammetry of all systems studied, implying fast electron-transfer kinetics. Changes in surface oxide coverage had little effect on kinetics, nor did the charge of the catechol species or the solution pH. Small ΔE_p values correlated with catechol adsorption, and surface pretreatments that decreased adsorption also increased ΔE_p. Electron transfer from catechols was profoundly inhibited by a monolayer of nitrophenyl or (trifluoromethyl)phenyl (TFMP) groups on the GC surface, so that voltammetric waves were not observed. The ΔE_p increased monotonically with surface coverage of TFMP groups. The results indicate that catechol adsorption to GC is required for fast electron transfer for the redox systems studied. Unlike $Ru(NH_3)_6^{3+/2+}$, chlorpromazine, methyl viologen, and several others, electron tunneling through monolayer films was not observed for the catechols. The results are not consistent with an electron-transfer mechanism involving proton transfer or electrostatic interactions between the catechols and surface sites on the GC surface. The vital role of adsorption in the electron-transfer process is currently under study but appears to involve changes in the inner-sphere reorganization energy.

Quinone/hydroquinone redox systems have been studied extensively for several reasons, not the least of which is their biological importance.[1] Catecholamine neurotransmitters, quinone-based metabolic cofactors, and the fundamental electron-transfer properties of quinones have stimulated extensive examinations of quinone redox chemistry, in both aqueous and nonaqueous environments.[2−9] Of particular relevance here are studies of heterogeneous electron transfer between solid electrodes and catechols or quinones. Such studies are of fundamental importance to the electrochemical detection of catecholamines as well as to the broader questions about quinone redox chemistry. Notable examples from the literature are the detailed examination of quinone reduction on platinum in aqueous buffers,[7] the oxidation of catechols on carbon paste,[2,3] and the dramatic effects of adsorbates on quinone electrochemistry on platinum and iridium electrodes.[5,6,8] These experiments provide an excellent description of the elementary steps comprising the 2 H^+, 2 e^- reduction of an *o*- or *p*-quinone to the corresponding hydroquinone and account for much of the pH dependence of the observed redox potential and kinetics. However, the dependence of quinone redox kinetics on the state of the electrode surface is much less well understood, particularly for widely used electroanalytical sensors based on glassy carbon (GC) or carbon fibers.

Many surface treatments of both Pt and carbon electrodes have demonstrated that the electrode surface has a profound effect on catechol voltammetry, with apparently minor changes to the surface causing large changes in electrode kinetics. For example, anodization of GC greatly decreases ΔE_p for dopamine (DA) and increases its adsorption.[9−12] However, laser activation also greatly decreases ΔE_p, with no apparent surface oxidation.[13,14] Fast DA kinetics may be observed on carbon surfaces with low or high oxygen/carbon (O/C) ratio, with or without anodization, and in certain cases on heavily modified electrodes (e.g., Nafion coated).[14] Many hypotheses for the pronounced sensitivity of DA kinetics to surface condition have been proposed, including ionic effects related to surface oxides,[11] proton transfer from oxide sites accompanying electron transfer,[10] and electrocatalysis by adsorption to the Pt or carbon surface.[1] For the case of clean Pt electrodes, irreversible adsorption of catechols and hydroquinones

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10.1021/ac990399d CCC: $18.00
Published on Web 09/09/1999

occurs, and this chemisorbed layer does not undergo reversible 2 e^- transfer to the corresponding quinone. However, chemically reversible electron transfer was observed on the irreversibly adsorbed organic layer.[5,6] For iridium surfaces, an oxide layer was found to inhibit the H_2Q/Q electron transfer, but the inhibition was reversed by small amounts of chemisorbed sulfur or iodide.[8] For either carbon or metal electrodes the oxidation of catechol to quinone involves 2 e^- and usually 2 H^+, so adsorbed species could affect one or more of four possible steps.[2,7]

We reported previously on a procedure for diagnosing surface effects on electrode kinetics, for the case of GC electrodes in aqueous solution.[16,17] The approach involved specific modifications to GC surfaces, followed by assessment of their effects on electrode kinetics for selected redox systems. Of note is the observation that several common redox systems are insensitive to surface modification (e.g., $Ru(NH_3)_6^{3+/2+}$, methyl viologen) and the observed rates are controlled by electron tunneling.[16,18] In contrast, several redox reactions (e.g., $Fe^{3+/2+}$) are catalyzed by certain surface groups and are very dependent on surface preparation.[17,19] The approach has been applied to a variety of inorganic[16] and organic[18] redox systems, but with the exception of ascorbic acid, none of these involved protons or multielectron transfer. In the current work, several catechols and hydroquinone were examined with the same approach, not only to extend our understanding of carbon electrode behavior but also to provide new insights into quinone electron-transfer mechanisms.

EXPERIMENTAL SECTION

Electrodes used include commercial GC electrodes from Bioanalytical Systems, Inc. (West Lafayette, IN) and disks cut from Tokai GC-20 plates. The disks were mounted in a homemade Teflon electrode holder after polishing or modification. All electrodes were polished before any surface treatments in 1-, 0.3-, and 0.05-μm alumina powders (Buehler, Lake Bluff, IL) slurried with Nanopure water (Barnstead Nanopure System, Dubuque, IA) on Microcloth polishing cloth (Buehler, Lake Bluff, IL) according to previously published procedures.[16,17,20] The electrodes were polished in each slurry for 2 min, with sonication for 10 min following the polishing procedure. Areas for both types of electrodes were determined by chronoamperometry. Static contact angles for Nanopure water were determined with a conventional contact angle microscope (Rame-Hart) in air.

Pyridine-treated surfaces were prepared by immersing a polished electrode in pyridine (Mallinckrodt, Inc.), heating the pyridine for 5 min to a temperature of approximately 65 °C, and then allowing the electrode to soak for 1 h while the pyridine cooled. The electrodes were rinsed thoroughly with Nanopure water and transferred to the electrochemical cell.

Methylene blue (MB) (Aldrich Chemical Co.) was adsorbed by two methods. The first follows the procedure described previously[17] involving adsorption of MB at high concentration (10 mM) and then transfer to catechol solution. In the second, MB and catechol were present simultaneously, as will be discussed in more detail later. Chemisorption of nitrobenzene and (trifluoromethyl)benzene was accomplished by the procedure of Savéant et al.[21] Diazonium salt solutions (1 mM) were reduced in 0.1 M tetrabutylammonium tetrafluoroborate in acetonitrile by voltammetric scans from +0.1 to −1.4 V vs Ag/Ag^+ at 200 mV/s until the reduction peak was absent (3 scans for nitrophenyl and 5−10 scans for trifluoromethyl phenyl derivatives).

Surfaces with low oxide coverage (as judged by O/C ratio from XPS) were prepared by anaerobic polishing in cyclohexane/alumina slurries on bare glass plates.[16] The cyclohexane was saturated with argon for 15−20 min before mixing with dry alumina. An alternative method for preparing low-oxide surfaces was vacuum heat treatment (VHT).[3,4,22] Briefly, the GC sample was heated (~800 °C) by resistive heating with a tantalum heating stub. After 30 min at ~800 °C in UHV, the sample was cooled and an XPS spectrum was acquired. Then the sample was quickly transferred in air to the electrochemical cell for voltammetry.

Cyclic voltammetry was carried out using a BAS 100/W electrochemical workstation. The reference electrode (Bioanalytical Systems Inc., West Lafayette, IN) used for aqueous work was a Ag/AgCl (3 M NaCl), and a Ag/Ag^+ reference was used for solutions in acetonitrile. A platinum wire was used as the counter electrode. Each voltammogram was recorded on a freshly prepared surface. Survey and regional XPS spectra were acquired with a VG Scientific Escalab MKII spectrometer with either Al or Mg anode. Grams32 (Galactic) software was used to calculate peak areas. Instrumental sensitivity factors were applied when calculating atomic ratios.

Catechol solutions were 1 mM unless otherwise noted and were prepared in either 0.1 M H_2SO_4 or 0.1 M PBS (0.1 M phosphate buffer with 0.1 M NaCl added). Dopamine and D,L-3,4-dihydroxyphenyl ethylene glycol (DOPEG) were used as received (Sigma). 4-Methylcatechol (4MC, Sigma) was recrystallized from toluene, and 3,4-dihydroxyphenylacetic acid (DOPAC, Sigma) was recrystallized from ethyl acetate/hexane. *p*-Nitrobenzenediazonium tetrafluoroborate and α,α,α-trifluorotoluenediazonium tetrafluoroborate were prepared according to Dunker et al.[23] Diazonium salt solutions (1 mM) were prepared in acetonitrile (Mallinckrodt Inc.) with 0.1 M tetrabutylammonium tetrafluoroborate (Fisher Scientific) as the supporting electrolyte.

RESULTS

Surface Preparation. Past experience in many laboratories indicates the importance of controlling surface chemistry when diagnosing electron-transfer mechanisms.[11,20,24,25] Accordingly, several preparations of GC electrodes that result in reasonably well-defined surfaces were employed here for examining quinone redox systems. These preparations were designed to modify particular surface properties, such as oxide coverage, carbon

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Table 1. XPS, Contact Angle, and Kinetic Results for Modified GC Surfaces[a]

		atomic ratio			
	contact angle (deg)	O/C	F/C	N/C	$k°$ (cm/s) $Fe(CN)_6^{3-/4-}$
polished	30 ± 3 (16)	0.12 ± 0.03 (8)			0.076 ± 0.007 (3)
pyridine treated	31 ± 4 (14)	0.07 ± 0.01 (4)			0.15 ± 0.02 (3)
low oxide (anaerobic polishing)	59 ± 3 (15)	0.04			
low oxide (VHT)	55 ± 7 (6)	0.04			0.14,[22] 0.07 [16]
MB modified (Γ = 328 pmol/cm^2)					0.078 ± 0.005
nitrophenyl modified	41 ± 2 (15)	0.21 ± 0.02 (4)		0.07 ± 0.01 (4)	0.01
TFMP modified	91 ± 4 (21)	0.03 ± 0.006 (4)	0.30 ± 0.01 (4)		
hydrogenated GC[28]	65	0.036			0.049

[a] Values in parentheses, number of experiments.

substrate exposure, and levels of physi- or chemisorbed surface species. The GC surfaces considered are listed in Table 1, along with contact angle for H_2O, and surface composition determined by XPS.

"Conventional" polishing in Al_2O_3/Nanopure slurries produced a 8−15% O/C ratio and exhibited a $k°$ for the benchmark $Fe(CN)_6^{3-/4-}$ system (1 M KCl) of 0.076 ± 0.007 cm/s. Polishing with Al_2O_3/H_2O preceded all other electrode treatments and will be considered a baseline surface for comparison. Pretreatment in pyridine lowered the O/C ratio and increased the observed $k°$ for $Fe(CN)_6^{3-/4-}$, apparently due to removal of adsorbed polar impurities. No residual nitrogen was revealed on the pyridine-treated surface by XPS. The $k°$ of 0.15 cm/s for $Fe(CN)_6^{3-/4-}$ is comparable to that obtained after treatment with other purified solvents and to that observed after ultraclean polishing[24] or vacuum heat treatment.[22,26] As shown in Figure 1, pyridine pretreatment decreased ΔE_p for 4MC and increased adsorption. The voltammograms obtained at low 4MC concentration (Figure 1, lower panel) are dominated by adsorbed 4MC as opposed to diffusing 4MC, and a pronounced increase in adsorption is apparent after pyridine pretreatment. The similarity of the adsorption on the pyridine-treated surface to that observed for GC, which was exposed to solution by fracturing,[9] implies that pyridine removes surface impurities from the polished surface and permits greater adsorption. Semiintegration of the voltammogram obtained for 1 mM 4MC after background subtraction confirmed 4MC adsorption, exhibiting a peak superimposed on a sigmoid.[27] 4MC was removed from GC surfaces by treatment with pyridine or isopropyl alcohol and followed a Langmuir isotherm in 0.1 M H_2SO_4. Behavior similar to that shown in Figure 1 was observed for DA and DOPAC at both 10 μM and 1 mM concentrations. The consequences of catechol adsorption are discussed in more depth later.

Oxygen-containing functional groups are often invoked to explain kinetic effects of GC pretreatments.[11,20] To assess their importance, GC electrodes with low O/C ratios were prepared by two methods. Anaerobic polishing in cyclohexane/Al_2O_3 slurries reduced the O/C to ~4%, as reported elsewhere.[16] Vacuum heat treatment (800 °C, $<10^{-8}$ Torr) yielded surfaces with O/C ratios in the range of 2−4%. These surfaces were used for voltammetry immediately after exposure to air, and previous results demonstrated that the O/C ratio increases slowly with air exposure time.[16] Hydrogen plasma-treated GC is included in Table 1, based on a separate report.[28]

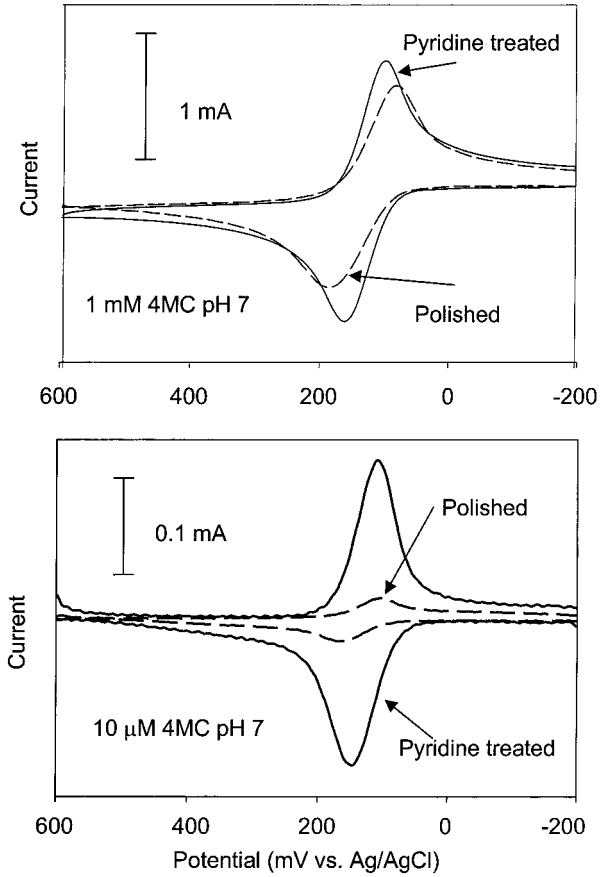

Figure 1. Voltammetry of 4-methylcatechol on polished GC (dashed) and pyridine-treated GC (solid line) at pH 7 with a scan rate of 1 V/s. Upper plot is for 1 mM 4MC solution; lower is for 10 μM 4MC. Note change in current scale between the two plots.

Controlled coverages of physi- or chemisorbed molecules on GC provide a means to reduce the area of the GC substrate exposed to the solution. Methylene blue was used as a physisorbed species, because it has been characterized previously[17] and because its voltammetric peaks may be observed simultaneously with those of the catechols. Isotherms for MB adsorption on polished GC before and after pyridine treatment are shown in

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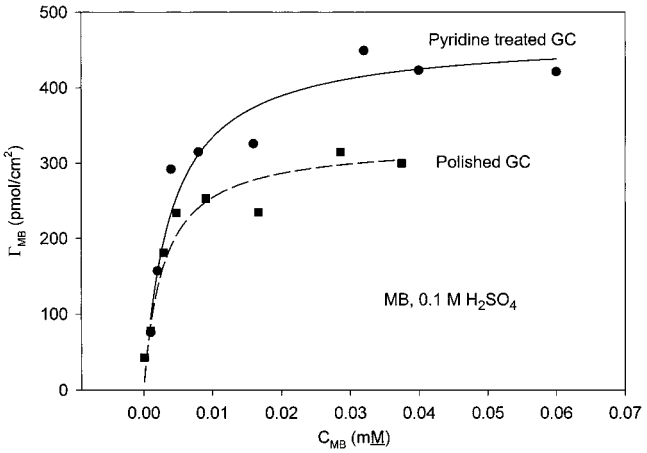

Figure 2. Isotherms for methylene blue adsorption on polished and pyridine-treated GC. Γ_{MB} determined from MB voltammetric peak area and geometric GC area. Solid line is fit of pyridine results to Langmuir equation, with $\Gamma_{sat} = 467$ pmol/cm^2 and $r^2 = 0.933$. Dashed line is fit to polished GC results, with $\Gamma_{sat} = 328$ pmol/cm^2 and $r^2 = 0.940$.

Figure 2, based on surface coverages calculated from the MB voltammetric peak area and the geometric area. While these curves show some scatter, they may be fit to the Langmuir equation with reasonable accuracy. Saturation coverage is reached at ~20 μM solution concentration, with a higher saturation coverage for the pyridine-treated surface (425 pmol/cm^2) than the polished surface (315 pmol/cm^2), both based on geometric area. These values are higher than those predicted from molecular geometry on a flat surface, due to the roughness factor of polished GC (in the range of 1.5−2.5 [29]). Previously, Raman spectroscopy revealed that MB adsorbs strongly to GC from 0.1 mM solutions and remains even after transfer to blank electrolyte.[17]

Monolayers of nitrophenyl (NP) and (trifluoromethyl)phenyl (TFMP) groups were formed on GC by reduction of the corresponding diazonium salt in acetonitrile.[21] It was necessary to thoroughly deaerate the CH_3CN for the TFMP case to achieve high coverage. XPS spectra for these two surfaces are shown in Figure 3. Previous reports on the NP-modified surface demonstrated formation of a compact monolayer observable with Raman spectroscopy.[30] The Raman cross section of the TFMP monolayer was too low to obtain a Raman spectrum, but the fluorine signal is strong in the XPS, and a distinct C_{1s} peak was observed for the TFMP carbon. An estimate of the TFMP coverage obtained by dividing the F/C ratio by 3 and assuming the carbon signal is due solely to GC yields a maximum coverage of 614 pmol/cm^2 of (trifluoromethyl)phenyl groups. As apparent in Table 1, the TFMP surface exhibited the highest contact angle for water observed here, 91°.

Electrode Kinetics. The GC surfaces described thus far fall into three general categories which serve to test various electron-transfer mechanisms. First, the polished and pyridine-treated surfaces have substantial oxide coverage (~7−12%) and varying level of adventitious impurities. Second, low-oxide surfaces (2−4% O/C) provide a test of the importance of oxygen-containing functional groups. The surfaces modified with MB, nitrophenyl, or (trifluoromethyl)phenyl monolayers comprise the third category, in which an intentional "spacer" is placed between the solution redox system and the GC substrate. To investigate the redox mechanisms of the catechols, the voltammetry of dopamine and related compounds was studied on the various pretreated surfaces.

Figure 4 compares the voltammograms of DA, 4MC, and DOPAC at pH 7 with that of $Ru(NH_3)_6^{3+/2+}$, for polished GC before and after derivatization with a nitrophenyl monolayer. While the monolayer has little effect on $Ru(NH_3)_6^{3+/2+}$, it profoundly inhibits electron transfer to DA, DOPAC, and 4MC. Similar effects were observed for DOPEG, and for all four catechols at pH 1 (Figure 5). The TFMP monolayer also inhibited catechol electron transfer, to the point where no Faradaic current was observed for saturation coverage by (trifluoromethyl)phenyl groups. Tables 2 and 3 list the observed ΔE_p values for these and other GC surfaces, at pH 7 and pH 1, respectively. The fluorine XPS signal for the TFMP surface provided a convenient marker for surface coverage, so the TFMP surface was examined in more detail. By reducing the duration of the applied potential during derivatization, the coverage of TFMP groups was decreased below saturation. Partial coverage of TFMP groups was indicated by a F/C ratio below 0.30. The voltammetry of DA on several such surfaces is shown in Figure 6. As the F/C ratio increases, indicating larger TFMP coverage, the ΔE_p increases, indicating slower electron transfer.

The effect of physisorbed MB on catechol voltammetry is shown in Figure 7 for the case of dopamine at pH 1.0. By varying the MB solution concentration, the MB coverage could be varied. Furthermore, the DA and MB voltammetric waves are distinct, so the MB coverage may be determined simultaneously with the ΔE_p for DA. As was observed for the TFMP monolayer, DA kinetics slow as MB coverage increases. Figure 8 shows the trend of ΔE_p with MB coverage for either the polished or pyridine-treated GC surfaces. While ΔE_p is smaller for the pyridine-treated surface, both show an increasing ΔE_p with MB coverage. As noted in Tables 2 and 3, all four catechols exhibited an increase in ΔE_p when MB was adsorbed on the GC surface.

The observed ΔE_p values for the polished, pyridine-treated, and low-oxide surfaces are also shown in Tables 2 and 3. Reduction of the surface O/C ratio has minor effects on ΔE_p. In fact, the VHT surface has the lowest O/C ratio of any of the surfaces studied here, but also the fastest kinetics, as judged from ΔE_p.

Hydroquinone and benzoquinone voltammetry was examined on polished and modified surfaces, for comparison to the catechols. The results listed in Table 4 show that both hydroquinone oxidation and benzoquinone reduction exhibit behavior similar to that of the catechols. Nitrophenyl and TFMP monolayers severely inhibit electron transfer, while the behavior on a low-oxide surface does not differ greatly from polished GC.

DISCUSSION

A cursory overview of the results leads to the immediate observation that the kinetics of all of the catechols studied behave similarly in response to surface modification and that some modifications have much greater effects on the catechols than others. Polishing, pyridine treatment, and VHT have relatively small effects on kinetics, with all four catechols and hydroquinone exhibiting ΔE_p values between 40 and 90 mV, with the exception of DOPAC at pH 7 (75−118 mV). While the effects of pyridine and VHT are real and will be discussed below, they are much

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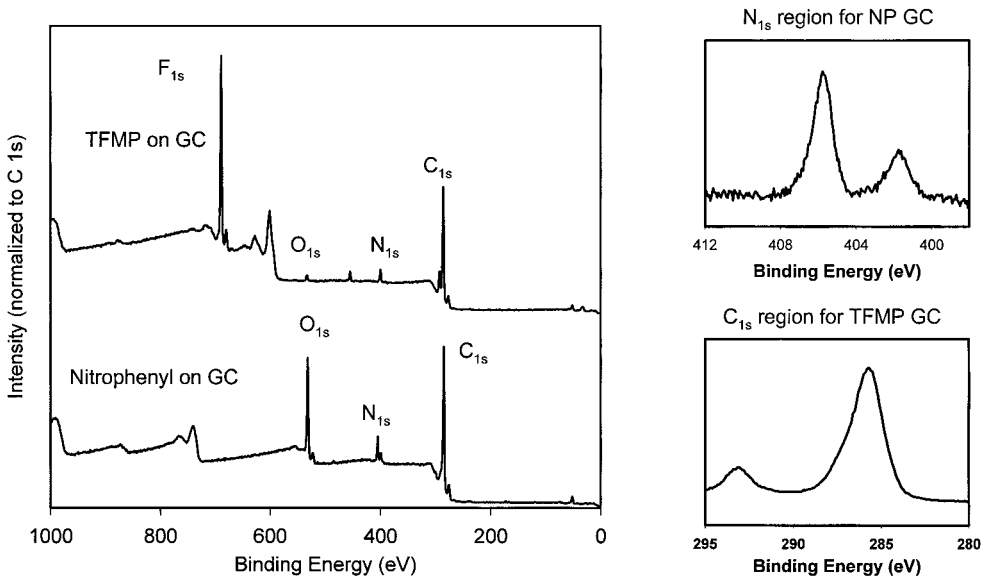

Figure 3. XPS spectra for nitrophenyl and TFMP monolayers on GC, following reduction of the corresponding diazonium salts. Spectra on the right side are high-resolution spectra of the N_{1s} and C_{1s} regions of the NP and TFMP surfaces, respectively.

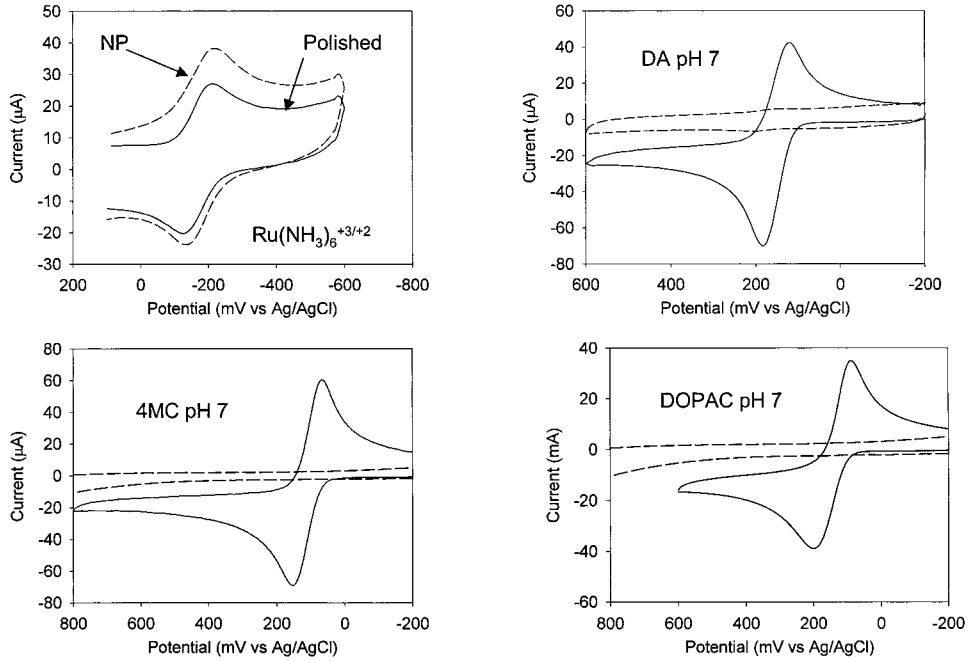

Figure 4. Voltammograms on polished GC (solid curves) and nitrophenyl-modified GC (dashed) for three catechols and $Ru(NH_3)_6^{3+/2+}$, all at 1 mM concentration. DA, 4MC, and DOPAC were in pH 7 buffer; $Ru(NH_3)_6^{3+/2+}$ was in 1 M KCl. Scan rate was 0.2 V/s for catechols and 20 V/s for $Ru(NH_3)_6^{3+/2+}$.

smaller than the effects of intentional adsorbed monolayers. For the NP and TFMP monolayers, the ΔE_p was at least 468 mV (4-methylcatechol at pH 7) and above 600 mV for all other catechols at either pH 1 or 7. On the basis of the early treatment of the relationship between ΔE_p and $k°$ by Nicholson,[31] an increase in ΔE_p from 53 to 468 mV (for 4MC) implies a decrease in $k°$ of a factor of ~4 orders of magnitude. This dramatic effect was not expected, since the same monolayers have small effects on $Ru(NH_3)_6^{3+/2+}$ kinetics (Table 2) and electron transfer to methyl viologen, methylene blue, and several phenothiazines.[16,18] The thin NP monolayer (~6.8 Å) has a relatively small effect on the tunneling rate, a factor of ~2 for these outer-sphere systems. These systems exhibit fast electron transfer on NP-modified surfaces because their electron transfer proceeds by electron tunneling through the adsorbed layer, similar to ferrocene on self-assembled monolayers.[32] The nearly complete inhibition of electron transfer from catechols and hydroquinone at the same modified GC surfaces raises the major question, why are quinones different from methyl viologen, the phenothiazines, and $Ru(NH_3)_6^{3+/2+}$? Why cannot the electron tunnel through the adsorbed layer in the case of catechols? To address these questions, the

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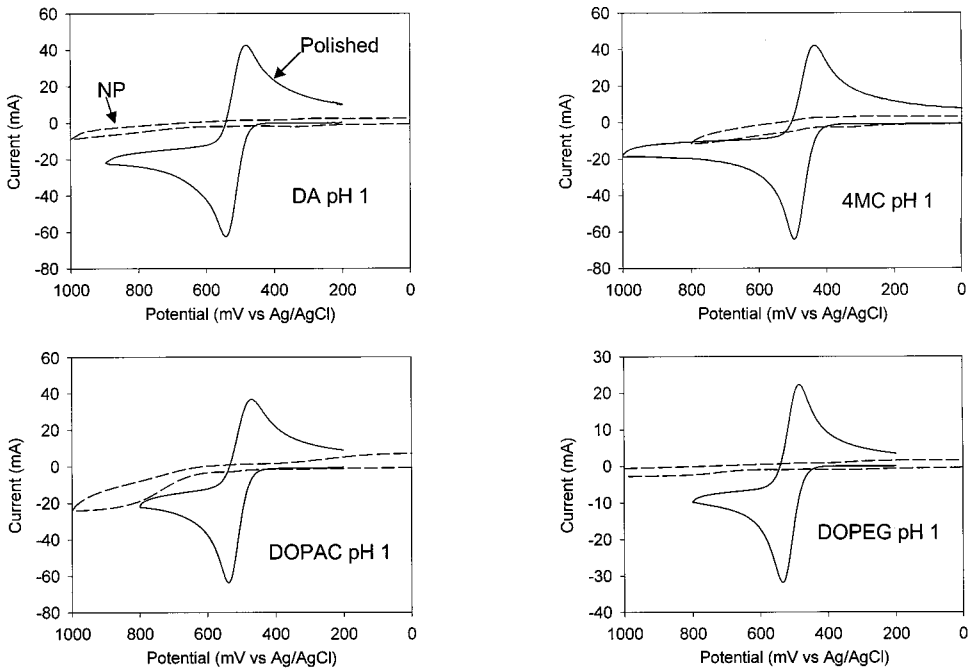

Figure 5. Voltammograms of four catechols on polished GC (solid curves) and nitrophenyl-modified GC (dashed). Conditions same as Figure 4, except medium was 0.1 M H_2SO_4 and DOPEG concentration was 0.4 mM.

Table 2. Peak Separations on GC Surfaces[a]

	ΔE_p (mV)[b]			
	DA	4MC	DOPAC	DOPEG
polished GC	67 ± 10 (6)	85 ± 18 (3)	115 ± 6 (3)	65 ± 3 (4) [76 ± 6 (3)][c]
pyridine treated	48 ± 3 (3)	53 (2)	75 ± 9 (4)	72 ± 2 (4)
low oxide (anaerobic polish)	88 ± 7 (3)	59 ± 2 (3)	118 (2)	[89 (2)]
low oxide (VHT)	[48]			
MB modified	193 ± 17 (3)	160 ± 11 (4)	274 ± 6 (3)	253 ± 3 (4)
NP modified	neg[d]	468 ± 6 (3)	none observable	>800 (4)
TFMP modified	>1000 (3)	>800 (3)	>1000 (3)	

[a] Conditions: 0.1 M pH 7 PBS; scan rate 200 mV/s. [b] Values in parentheses, number of experiments. [c] Values without brackets are for BAS electrodes. Bracketed values are for GC20 plates in a Teflon holder. [d] Indicates that only very small peaks were observed, not attributable to solution species.

Table 3. Peak Separation on GC Surfaces[a]

	ΔE_p (mV)[b]			
pH 1	DA	4MC	DOPAC	DOPEG
polished	61 ± 16 (6)	62 ± 7 (5)	61 ± 8 (5)	47 ± 4 (3) [53 ± 6 (4)][c]
pyridine treated	40 ± 4 (3)	50 ± 2 (4)	42 ± 4 (4)	40 ± 4 (3)
low oxide (anaerobic polish)	66 ± 4 (4)	81 ± 8 (4)	[70 ± 6 (4)]	[66 ± 3 (3)]
low oxide (VHT)	[40 ± 2 (3)]			
MB (modified)	287 ± 21 (5)	156 ± 4 (3)	208 ± 8 (3)	267 ± 18 (6)
NP (modified)	neg[d]	neg	>600 (3)	none observable
TFMP modified	none observable	neg	neg	

[a] Conditions: 0.1 M H_2SO_4, scan rate 200 mV/s. [b] Values in parentheses, number of experiments. [c] Values without brackets are for BAS electrodes. Bracketed values are for GC20 plates in a Teflon holder. [d] Indicates that only very small peak(s) observed, not attributable to solution species.

current results will be discussed in light of possible electron-transfer mechanisms. First, the effects of surface oxides and polishing will be considered and then the more dramatic consequences of adsorbed monolayers.

The pyridine-treated and low-oxide GC electrodes provide useful "baseline" surfaces for comparison to conventionally polished and modified surfaces. The decrease in ΔE_p for all of the catechols and for hydroquinone/benzoquinone compared to the polished surface implies an increase in electron-transfer rate due to removal of polishing debris or impurities. The increased adsorption of both MB and DA on the pyridine-treated surfaces further supports the conclusion that pyridine is removing adventi-

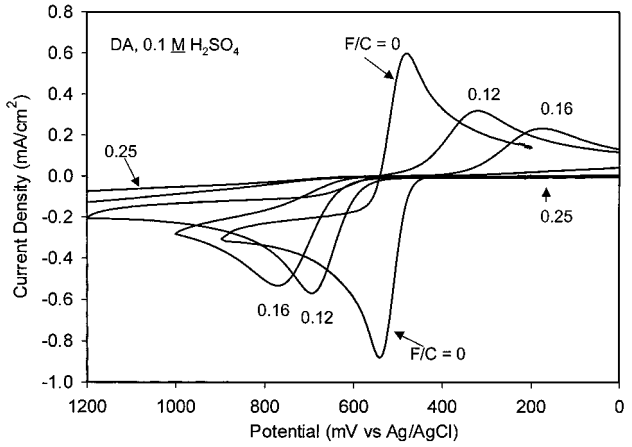

Figure 6. Voltammograms of 1 mM dopamine in 0.1 M H_2SO_4 (0.2 V/s) on GC with varying coverages of TFMP monolayer. Numbers accompanying each curve are the atomic F/C ratio observed by XPS for each surface.

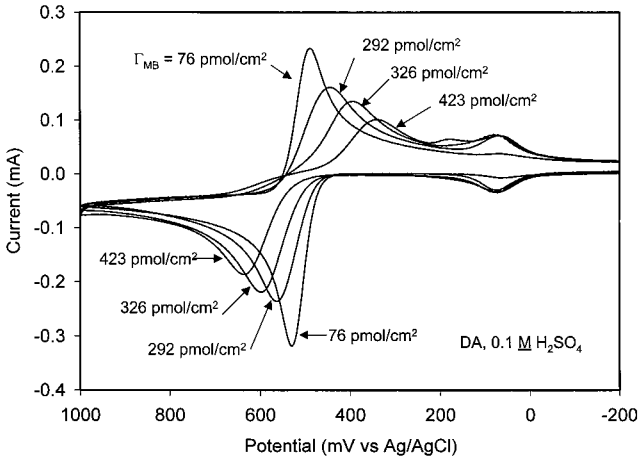

Figure 7. Voltammograms of 1 mM DA in 0.1 M H_2SO_4 on pyridine-treated GC (0.2 V/sec) containing varying concentrations of MB. Numbers accompanying curves are the MB surface coverages calculated from the MB adsorption peak at ~100 mV vs Ag/AgCl.

tious impurities and exposing a larger GC surface for catechol or MB adsorption. A recent report[33] on pretreatment of GC with purified solvents (e.g., 2-propanol, acetonitrile) demonstrated similar increases in adsorption and apparent electron-transfer rates for DA and several other redox systems. Furthermore, the observed ΔE_p for DA following pyridine treatment is comparable to that for vacuum heat treatment (48 mV) and slightly greater than ΔE_p for DA after laser activation (32 mV)[13] and fracturing in solution (28 mV).[9] While it is true that these ΔE_p values are perturbed by DA adsorption, they do indicate that pyridine treatment produces a GC surface that is reactive toward adsorption and electron transfer. Not only does pyridine yield a lower ΔE_p than the majority of pretreatments reported in the literature but the ΔE_p is as small as that observed for more complex pretreatments such as VHT. In the context of the current report, the pyridine treatment yields a GC surface that is more reactive toward adsorption and electron transfer than the conventionally polished surface and that serves as benchmark for a clean GC surface.

Reduction of the surface O/C ratio by anaerobic polishing or VHT has fairly minor effects on catechol and hydroquinone

(33) Ranganathan, S.; Kuo, T.-C.; McCreery, R. L., submitted to *Anal. Chem.*.

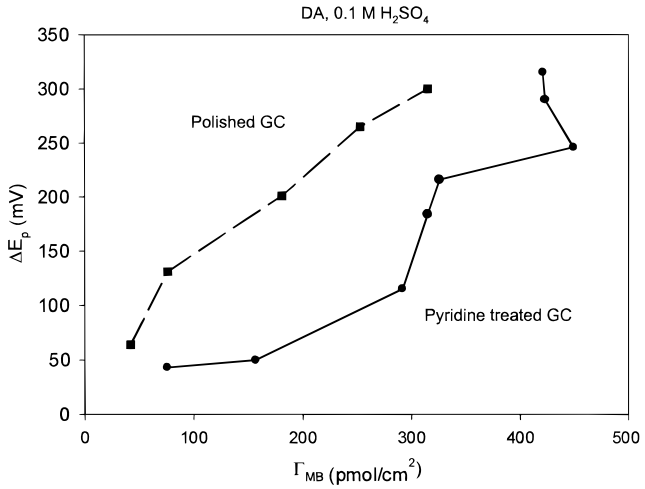

Figure 8. Trends of ΔE_P for DA (0.2 V/s, 0.1 M H_2SO_4) as functions of MB surface coverage on polished GC (dashed line) and pyridine-treated GC (solid line). Γ_{MB} determined from peak area of MB surface peak, shown in Figure 7.

Table 4. Peak Separations on Modified GC Surfaces

	ΔE_p (mV)[b]	
	pH 7	pH 1
(A) For 1 mM *p*-Benzoquinone		
polished	81 ± 4 (5)	50 ± 2 (4)
pyridine treated		45 ± 1 (4)
low oxide (anaerobic polish)		67
MB (modified)	220 ± 15 (3)	162 ± 7 (4)
NP (modified)	469	
TFMP modified	654	703
(B) For 1 mM hydroquinone		
polished	82 ± 2 (3)	61 ± 6 (5)
pyridine treated	66 ± 1 (3)	53 ± 5 (4)
low oxide (anaerobic polish)	59 ± 2 (3)	58 ± 1 (3)
low oxide (VHT)	[61]	
MB (modified)	221 ± 28 (3)	200 ± 14 (4)
NP (modified)	493	>800
TFMP modified	>1000	>850

[a] Scan rate, 200 mV/s. [b] Values in parentheses, number of experiments.

kinetics. The cyclohexane/Al_2O_3 polish reduced the surface O/C to 0.04 and yields generally larger ΔE_p values than the pyridine treatment. However, the VHT surface, with even lower O/C (0.02−0.04) had a ΔE_p comparable to the pyridine-treated surface with an O/C of 0.07. Although the variability in surface oxide effects on different catechols makes it difficult to deduce kinetic consequences of surface oxides, it is clear that surface O/C and electron-transfer rates are not correlated with any consistency. For both pH 1 and pH 7, and for catechols that are neutral, cationic, and anionic, changing the surface O/C can both increase and decrease ΔE_p. For the case of hydroquinone, lowering the O/C ratio had virtually no effect on ΔE_p. Combined with the observations that dopamine kinetics are quite fast on hydrogen-terminated GC (O/C ~0.01) and on GC fractured in solution, these observations lead to the conclusion that electron-transfer kinetics for the catechols and hydroquinone on GC are largely independent of the coverage of oxygen-containing functional groups, at least for the surfaces considered here.

Although surface oxides do not correlate with electron-transfer kinetics between GC and the catechols, there is a strong correlation between catechol adsorption and kinetics. ΔE_p increases monotonically with the coverage of MB or (trifluoromethyl)phenyl groups on the surface (Figure 8). If the surface is pretreated with pyridine, both adsorption and electron-transfer rate increase. These effects are much too large to be explained by adsorption-induced distortion of the voltammograms, which would cause some decrease in ΔE_p with no change in k° in the presence of adsorption. The NP and TFMP monolayers completely shut off electron-transfer, even to freely diffusing catechols. The correlation between adsorption and electron transfer raises two possibilities (at least) for the electron-transfer mechanism. Adsorption itself may be required as a step in the overall electron-transfer reaction. Alternatively, the monolayers that prevent adsorption may also block some other process that is essential to electron transfer, such as proton transfer or redox mediation. The results definitely establish that electron tunneling is insufficient for catechol oxidation (or quinone reduction), in contrast to the results for the phenothiazines and several inorganic redox systems such as $Ru(NH_3)_6^{3+/2+}$.

Past investigations of quinone electron transfer have resulted in several hypotheses for surface effects on kinetics, including redox mediation, proton transfer to surface sites, hydrophobic effects, and ionic attraction or repulsion between the catechol and a surface charge. While such effects should be blocked by a NP or TFMP monolayer, they are otherwise inconsistent with the current results. A redox mediation mechanism should depend strongly on the $E^{\circ\prime}$ of the catechol relative to that of the mediator,[4] yet the effects observed here are consistent for different $E^{\circ\prime}$ values and pH. Furthermore, surface-bound redox mediators would probably contain oxygen, and the kinetic effects are largely independent of O/C ratio. Proton-transfer catalysis accompanying electron transfer should also depend on surface oxides to provide surface sites to accept or donate protons.[10] In addition, the change in pH from 1 to 7 should alter the order of proton and electron transfer from eHeH for oxidation at pH 1 to HeHe for oxidation at pH 7.[2,3,7] If proton transfer were rate limiting, one would expect significant voltammetric changes with pH and with the direction of the reaction (oxidation or reduction). In fact, previous workers accounted for the redox behavior of the hydroquinone/quinone system on carbon paste and platinum by assuming proton transfers were at equilibrium throughout the redox process.[1,2,3,7] The contact angle data in Table 1 indicate that surfaces with similar hydrophobicity (e.g., polished GC and nitrophenyl-modified GC) have very different kinetics. There is no correlation between contact angle and electron-transfer rate, so hydrophobic effects do not solely account for variations in ΔE_p. Finally, the effects of neutral (NP, TFMP) or cationic (MB) adsorbates are similar for catechols that are neutral (4MC, DOPEG), cationic (DA), or anionic (DOPAC at pH 7), indicating that electrostatic effects cannot account for the large kinetic effects. Such effects account for relatively small kinetic effects through Frumkin corrections,[34] but these are factors of 2 or 3, not several orders of magnitude. Heavily oxidized carbon surfaces, or polished surfaces coated with Nafion,[12,15] have been shown to enhance voltammetric response to cations (e.g., DA) while suppressing response to anions (DOPAC, ascorbate, $Fe(CN)_6^{3-/4-}$). Such enhancements are clearly due to electrostatic effects and result from preconcentration of cations by sorption into the anionic film on the oxidized or Nafion-treated carbon surface. However, this effect is not of major significance for the surfaces studied here. For the VHT, fractured, and polished GC, the observed ΔE_p is independent of the charge on the catechol. For the case of adsorbed MB (a cation) and DOPAC (an anion at pH 7), the rate is actually *slower* than dopamine (a cation), a result opposite to that predicted from electrostatic considerations. Furthermore, small ΔE_P and fast kinetics were observed for the low-oxide surface without regard to redox system or surface charge, ruling out significant catalysis by electrostatic interactions.

After ruling out several events such as proton transfer, redox mediation, and interactions with surface oxides as being of major importance to catechol kinetics on clean, low-oxide GC surfaces, we are left with several consistent observations about the factors that control catechol kinetics on glassy carbon. First, all catechols studied adsorb to unmodified GC at both low and neutral pH. Second, methylene blue, nitrophenyl, and TFMP monolayers inhibit catechol adsorption, as was observed for phenothiazines and methyl viologen.[18] Third, catechol adsorption tracks electron-transfer kinetics (as judged by ΔE_p), for pyridine-cleaned GC and GC modified with MB, NP, or TFMP monolayers. The changes in ΔE_p accompanying inhibition of adsorption are much too large to be explained by a transition from adsorbed to diffusing reactants. Fourth, adsorption and electron-transfer kinetics do *not* correlate with surface oxide level, at least for the range of oxide coverage studied here (2−12%). This observation is consistent with the report that GC exposed in solution by fracturing shows comparably fast kinetics for DA, DOPAC, and 4MC.[9] Fifth, catechol oxidation is completely suppressed by a monolayer of NP or TFMP groups, indicating that electron tunneling through the monolayer is very slow, unlike the cases of $Ru(NH_3)_6^{3+/2+}$, chlorpromazine, methyl viologen, ferrocene, etc. For the case of the phenothiazines, a monolayer suppresses adsorption, but has little effect on electron-transfer rate, in complete contrast to the catechols.[18]

The effects of adsorption on quinone electron transfer on platinum, many of which were reviewed by Chambers,[1] provide some parallel to the current observations. Cyanide adsorption on Pt greatly decreases electron-transfer rates to quinones, even though electron tunneling through a cyanide layer would be expected to be efficient. Soriaga et al. found that an oxide film on iridium greatly inhibited H_2Q/Q electron transfer, but a low coverage of sulfur (∼10%) restored the rate to near-reversibility.[8] Electron-transfer mechanisms on metals may differ from that on GC, but the Pt and Ir results are consistent with the conclusion that surface monolayers may inhibit electron transfer by preventing quinone adsorption, rather than by significantly affecting electron tunneling.

So why is adsorption required for fast kinetics for the catechols and hydroquinone on GC, but not for methyl viologen, chlorpromazine, etc.? According to several authors, the catechol/orthoquinone and benzoquinone/hydroquinone redox systems follow the "scheme of squares", with two electron-transfer steps interspersed with fast proton transfers.[2,3,7] NP or TFMP monolayers

(34) Deakin, M. R.; Stutts, K. J.; Wightman, R. M. *J. Electroanal. Chem.* **1985**, *182*, 113.

may inhibit either or both of the electron-transfer steps, resulting in the behavior shown in Figures 5 and 6. A strong possibility for catechol behavior is that unlike methyl viologen, chlorpromazine, and ferrocene, hydroquinones must undergo significant bond length changes during oxidation or reduction.[1] The nuclear motion involved should result in a large inner-sphere reorganization energy and accompanying slow kinetics. It is quite possible that adsorption reduces this reorganization energy by inducing some or all of the required nuclear motion. We are currently investigating which of the two electron transfers is most affected by adsorption, and the correlation of this effect with changes in molecular geometry.

This work was supported by the NSF Division of Analytical and Surface Chemistry. Useful conversations with James Chambers, Greg Swain, and Mark Wightman were appreciated by the authors.

Received for review April 19, 1999. Accepted August 2, 1999.

AC990399D