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 $\Delta E_p$ values compared to cyclic voltammetry of all systems studied, implying fast electron-transfer kinetics. Changes in surface oxide coverage had little effect on kinetics, nor did the surface coverage of TFMP increase monotonically with surface coverage of TFMP. 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.

Many hypotheses for the pronounced sensitivity of DA kinetics to surface condition have been proposed, including ionic effects 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 electron transfer, with apparently minor changes to the surface causing large changes in electrode kinetics. For example, anodization of GC greatly decreases $\Delta E_p$ for dopamine (DA) and increases its adsorption. However, laser activation also greatly decreases $\Delta E_p$ with no apparent surface oxidation. 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). M any hypotheses for the pronounced sensitivity of DA kinetics to surface condition have been proposed, including ionic effects related to surface oxides, proton transfer from oxide sites accompanying electron transfer, and electrocatalysis by adsorption to the Pt or carbon surface.

For the case of clean Pt electrodes, irreversible adsorption of catechols and hydroquinones accompanies electron transfer, with apparently minor changes to the surface causing large changes in electrode kinetics. For example, anodization of GC greatly decreases $\Delta E_p$ for dopamine (DA) and increases its adsorption. However, laser activation also greatly decreases $\Delta E_p$ with no apparent surface oxidation. 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). Many hypotheses for the pronounced sensitivity of DA kinetics to surface condition have been proposed, including ionic effects related to surface oxides, proton transfer from oxide sites accompanying electron transfer, and electrocatalysis by adsorption to the Pt or carbon surface.

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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. For iridium surfaces, an oxide layer was found to inhibit the H2O/Q electron transfer, but the inhibition was reversed by small amounts of chemisorbed sulfur or iodide. 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(NH3)63+/2+, methyl viologen) and the observed rates are controlled by electron tunneling. In contrast, several redox reactions (e.g., Fe3+/2+) are catalyzed by certain surface groups and are very dependent on surface preparation.18,19 The approach has been applied to a variety of inorganic16 and organic18 redox systems, but with the exception of ascorbic acid, none of these involved protons or multielectron transfers.2,7

Previously 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 Saveant et al. 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 anodeforming in cyclohexane/alumina slurries on bare glass plates. 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). 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 H2SO4 or 0.1 M PBS (0.1 M phosphate buffer with 0.1 M NaCl added). Dopamine and dopamine-related compounds were purchased from Sigma-Aldrich Chemical Co. (Milwaukee, WI) and recrystallized from ethyl acetate or toluene. 4-Methylcatechol (4MC) was recrystallized from ethyl acetate/hexane. α,α,α-Trifluorotoluenediazonium tetrafluoroborate (TETFB) was prepared according to Dunker et al.32 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.2,20,22,25 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

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) slurred with Nanopure water (Barnstead Nanopure System, Dubuque, IA) on M microcloth polishing cloth (BUehler, Lake Bluff, IL) according to previously published procedures.26,27,28 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 chronocoulometry. 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.

M ethylene blue (MB) (Aldrich Chemical Co.) was adsorbed by two methods. The first follows the procedure described

substrate exposure, and levels of physi- or chemisorbed surface species. The GC surfaces considered are listed in Table 1, along with contact angle for H₂O, and surface composition determined by XPS.

“Conventional” polishing in Al₂O₃/Nanopure slurries produced a 8–15% O/C ratio and exhibited a k° for the benchmark Fe(CN)₆³⁻/⁴⁻ system (1 M KCl) of 0.076 ± 0.007 cm/s. Polishing with Al₂O₃/H₂O 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)₆³⁻/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)₆³⁻/⁴⁻ is comparable to that obtained after treatment with other purified solvents and to that observed after ultraclean polishing or vacuum heat treatment. As shown in Figure 1, pyridine pretreatment decreased $E_p$ 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, implies that pyridine removes surface impurities from the polished surface and permits greater adsorption. 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. To assess their importance, GC electrodes with low O/C ratios were prepared by two methods. Anaerobic polishing in cyclohexane/Al₂O₃ slurries reduced the O/C to 4%, as reported elsewhere. 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. Hydrogen plasma-treated GC is included in Table 1, based on a separate report.

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 and because its voltammetric peaks may be observed simultaneously with those of the catechols. Isotherms for M adsorption on polished GC before and after pyridine treatment are shown in

![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 10⁻⁶ M 4MC. Note change in current scale between the two plots.](image)

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

<table>
<thead>
<tr>
<th>Surface Type</th>
<th>Contact Angle (deg)</th>
<th>O/C Ratio</th>
<th>F/C Ratio</th>
<th>N/C Ratio</th>
<th>k° (cm/s) Fe(CN)₆³⁻/⁴⁻</th>
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<tr>
<td>polished</td>
<td>30 ± 3 (16)</td>
<td>0.12 ± 0.03 (8)</td>
<td></td>
<td></td>
<td>0.076 ± 0.007 (3)</td>
</tr>
<tr>
<td>pyridine treated</td>
<td>31 ± 4 (14)</td>
<td>0.07 ± 0.01 (4)</td>
<td></td>
<td></td>
<td>0.15 ± 0.02 (3)</td>
</tr>
<tr>
<td>low oxide (anaerobic polishing)</td>
<td>59 ± 3 (15)</td>
<td>0.04</td>
<td></td>
<td></td>
<td>0.14 ± 0.07</td>
</tr>
<tr>
<td>low oxide (VHT)</td>
<td>55 ± 7 (6)</td>
<td>0.04</td>
<td></td>
<td></td>
<td>0.078 ± 0.005</td>
</tr>
<tr>
<td>MB modified (T = 328 pmol/cm²)</td>
<td>41 ± 2 (15)</td>
<td>0.21 ± 0.02 (4)</td>
<td></td>
<td></td>
<td>0.07 ± 0.01 (4)</td>
</tr>
<tr>
<td>Nitrophenyl modified</td>
<td>91 ± 4 (21)</td>
<td>0.03 ± 0.006 (4)</td>
<td>0.30 ± 0.01 (4)</td>
<td></td>
<td>0.01</td>
</tr>
<tr>
<td>TFMP modified</td>
<td>65</td>
<td>0.036</td>
<td></td>
<td></td>
<td>0.049</td>
</tr>
<tr>
<td>Hydrogenated GC²⁸</td>
<td></td>
<td></td>
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</tbody>
</table>

² Values in parentheses, number of experiments.

Figure 2. Isotherms for methylene blue adsorption on polished and pyridine-treated GC. $\Gamma_{\text{MB}}$ determined from MB voltammetric peak area and geometric area. Solid line is fit of pyridine results to Langmuir equation, with $\Gamma_{\text{sat}} = 467$ pmol/cm$^2$ and $r^2 = 0.933$. Dashed line is fit to polished GC results, with $\Gamma_{\text{sat}} = 328$ 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 $\sim 20 \mu M$ 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$^\text{a}$). Previously, Raman spectroscopy revealed that MB adsorbs strongly to GC from 0.1 mM solutions and remains even after transfer to blank electrolyte.$^\text{c}$

Monolayers of nitrophenyl (NP) and (trifluoromethyl)phenyl (TFMP) groups were formed on GC by reduction of the corresponding diazonium salt in acetonitrile.$^\text{b}$ It was necessary to thoroughly deaerate the CH$_3$CN 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.$^\text{b}$ 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 C1s 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,$^\text{c}$

**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 ($\sim 7–12\%$) 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 $\Delta E_p$ values for these and other GC surfaces, at pH 7 and pH 1, respectively. The fluorescent 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 $\Delta E_p$ 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 $\Delta E_p$ for DA. As was observed for the TFMP monolayer, DA kinetics slow as MB coverage increases. Figure 8 shows the trend of $\Delta E_p$ with MB coverage for either the polished or pyridine-treated GC surfaces. While $\Delta E_p$ is smaller for the pyridine-treated surface, both show an increasing $\Delta E_p$ with MB coverage. As noted in Tables 2 and 3, all four catechols exhibited an increase in $\Delta E_p$ when MB was adsorbed on the GC surface.

The observed $\Delta E_p$ 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 $\Delta E_p$. 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 $\Delta E_p$.

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 $\Delta E_p$ 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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smaller than the effects of intentional adsorbed monolayers. For
the NP and TFMP monolayers, the $\Delta E_p$ 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 $\Delta E_p$ and $k^\circ$ by Nicholson, an increase in
$\Delta E_p$ from 53 to 468 mV (for 4MC) implies a decrease in $k^\circ$ of a
factor of ~4 orders of magnitude. This dramatic effect was not
expected, since the same monolayers have small effects on
$\text{Ru(NH}_3\text{)}_6^{3+/2+}$ kinetics (Table 2) and electron transfer to methyl
viologen, methylene blue, and several phenothiazines. 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 sur-
faces because their electron transfer proceeds by electron tun-
neling through the adsorbed layer, similar to ferrocene on self-
assembled monolayers. The nearly complete inhibition of elec-
ton transfer from catechols and hydroquinone at the same modi-
fied GC surfaces raises the major question, why are quinones dif-
f erent from methyl viologen, the phenothiazines, and $\text{Ru(NH}_3\text{)}_6^{3+/2+}$?
Why cannot the electron tunnel through the adsorbed
layer in the case of catechols? To address these questions, the

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 $\text{Ru(NH}_3\text{)}_6^{3+/2+}$, all at
1 mM concentration. DA, 4MC, and DOPAC were in pH 7 buffer; $\text{Ru(NH}_3\text{)}_6^{3+/2+}$ was in 1 M KCl. Scan rate was 0.2 V/s for catechols and 20 V/s
for $\text{Ru(NH}_3\text{)}_6^{3+/2+}$.

(32) Finklea, H. In Electroanalytical Chemistry; Bard, A. J., Rubinstein, I., Eds.;
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 $\Delta E_p$ 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 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$_2$SO$_4$ and DOPEG concentration was 0.4 mM.](image)

<table>
<thead>
<tr>
<th></th>
<th>DA</th>
<th>4MC</th>
<th>DOPAC</th>
<th>DOPEG</th>
</tr>
</thead>
<tbody>
<tr>
<td>polished GC</td>
<td>67 ± 10 (6)</td>
<td>85 ± 18 (3)</td>
<td>115 ± 6 (3)</td>
<td>65 ± 3 (4)</td>
</tr>
<tr>
<td>pyridine treated</td>
<td>48 ± 3 (3)</td>
<td>53 (2)</td>
<td>75 ± 9 (4)</td>
<td>72 ± 2 (4)</td>
</tr>
<tr>
<td>low oxide (anaerobic polish)</td>
<td>88 ± 7 (3)</td>
<td>59 ± 2 (3)</td>
<td>118 (2)</td>
<td>[89 (2)]</td>
</tr>
<tr>
<td>low oxide (VHT)</td>
<td>[48]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M B modified</td>
<td>193 ± 17 (3)</td>
<td>160 ± 11 (4)</td>
<td>274 ± 6 (3)</td>
<td>253 ± 3 (4)</td>
</tr>
<tr>
<td>NP modified</td>
<td>neg$^c$</td>
<td>468 ± 6 (3)</td>
<td>none observable</td>
<td>&gt;800 (4)</td>
</tr>
<tr>
<td>TFMP modified</td>
<td>&gt;1000 (3)</td>
<td>&gt;800 (3)</td>
<td>&gt;1000 (3)</td>
<td></td>
</tr>
</tbody>
</table>

*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>
<thead>
<tr>
<th>pH 1</th>
<th>DA</th>
<th>4MC</th>
<th>DOPAC</th>
<th>DOPEG</th>
</tr>
</thead>
<tbody>
<tr>
<td>polished</td>
<td>61 ± 16 (6)</td>
<td>62 ± 7 (5)</td>
<td>61 ± 8 (5)</td>
<td>47 ± 4 (3)</td>
</tr>
<tr>
<td>pyridine treated</td>
<td>40 ± 4 (3)</td>
<td>50 ± 2 (4)</td>
<td>42 ± 4 (4)</td>
<td>[53 ± 6 (4)]</td>
</tr>
<tr>
<td>low oxide (anaerobic polish)</td>
<td>66 ± 4 (4)</td>
<td>81 ± 8 (4)</td>
<td>70 ± 6 (4)</td>
<td>[66 ± 3 (3)]</td>
</tr>
<tr>
<td>low oxide (VHT)</td>
<td>[40 ± 2 (3)]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M B (modified)</td>
<td>287 ± 21 (5)</td>
<td>156 ± 4 (3)</td>
<td>208 ± 8 (3)</td>
<td>267 ± 18 (6)</td>
</tr>
<tr>
<td>NP (modified)</td>
<td>neg$^d$</td>
<td>neg</td>
<td>&gt;600 (3)</td>
<td>none observable</td>
</tr>
<tr>
<td>TFMP (modified)</td>
<td>none observable</td>
<td>neg</td>
<td></td>
<td></td>
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</tbody>
</table>

*Conditions: 0.1 M H$_2$SO$_4$, 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.*
tious impurities and exposing a larger GC surface for catechol or MB adsorption. A recent report 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 $\Delta E_p$ for DA following pyridine treatment is comparable to that for vacuum heat treatment (48 mV) and slightly greater than $\Delta E_p$ for DA after laser activation (32 mV) and fracturing in solution (28 mV). While it is true that these $\Delta E_p$ 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 $\Delta E_p$ than the majority of pretreatments reported in the literature but the $\Delta E_p$ 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 kinetics. The cyclohexane/Al$_2$O$_3$ polish reduced the surface O/C to 0.04 and yields generally larger $\Delta E_p$ values than the pyridine treatment. However, the VHT surface, with even lower O/C (0.02–0.04) had a $\Delta E_p$ 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 $\Delta E_p$. For the case of hydroquinone, lowering the O/C ratio had virtually no effect on $\Delta E_p$. 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. $\Delta E_p$ increases monotonically with the coverage of MB or (trifluoroacetyl) 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 voltamograms, which would cause some decrease in $\Delta E_p$ with no change in $k^o$ 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 $\text{Ru(NH}_3)_6^{3+/2+}$.

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 consistent with the current results. A redox mediation mechanism should depend strongly on the $E^o$ of the catechol relative to that of the mediator, yet the effects observed here are consistent for different $E^o$ 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 effects independent of O/C ratio. Proton-transfer catalysis 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. Ninth, 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 $\text{Ru(NH}_3)_6^{3+/2+}$, 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.

The effects of adsorption on quinone electron transfer on platinum, many of which were reviewed by Chambers, 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 $\text{H}_2\text{Q}/\text{Q}$ electron transfer, but a low coverage of sulfur (~10%) restored the rate to near-reversibility. 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? In consideration of a “scheme of squares”, with two electron-transfer steps interspersed with fast proton transfers, NP or TFMP monolayers...
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. 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.

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