Self-catalysis by Catechols and Quinones during Heterogeneous Electron Transfer at Carbon Electrodes

Stacy H. DuVall and Richard L. McCreery*

Contribution from the Department of Chemistry, Ohio State University, 100 W. 18th Street, Columbus, Ohio 43210-1185

Received January 21, 2000. Revised Manuscript Received May 10, 2000

Abstract: Heterogeneous electron transfer kinetics for several catechols were examined on glassy carbon (GC) electrodes in aqueous solution. Electrode preparations yielded GC surfaces with low levels of oxides or adsorbed impurities, which exhibited strong adsorption of dopamine (DA) and related catechols. Conversely, modification of GC with an organic monolayer suppressed DA adsorption and in many cases prevented electron transfer. By relating catechol adsorption to observed electron transfer, it was concluded that an adsorbed layer of catechol acts as an electrocatalyst for solution-phase redox components. Physisorbed or chemisorbed monolayers of several quinones, including duroquinone, anthraquinone, and dopamine itself, are catalytic toward dopamine oxidation and reduction, but nitrophenyl, trifluoromethylphenyl, and methylene blue monolayers severely inhibit electron transfer. The magnitude of inhibition was affected by electrostatic attraction or repulsion between the surface and the redox system, but the major factor controlling electron-transfer kinetics is not electrostatic in origin. The most plausible mechanism is "self-catalysis" by an adsorbed quinone, which remained adsorbed during electron transfer to a redox couple in solution. The results are inconsistent with a redox mediation mechanism involving a redox cross-reaction between adsorbed and solution quinone couples. An interaction between the adsorbed and solution quinone species during electron transfer appears to catalyze one or more of the steps in the "scheme of squares" mechanism for hydroquinone/quinone redox systems. The results explain a variety of observations about catechol and hydroquinone electrochemistry, as well as provide more fundamental insights into quinone electron-transfer mechanisms.

Introduction

The ortho and para quinone/hydroquinone redox systems have been studied extensively for at least three rather disparate reasons. First, quinones comprise a redox reaction of classical and current importance to organic chemistry and represent one of the oldest and most basic redox processes.[1−9] The order and kinetics of the two-electron/two-proton redox reactions continue to be active subjects of investigation.[4,7,10] Second, the role of catecholamines in neurochemistry has stimulated widespread effort related to their electrochemical analysis, particularly for monitoring neurotransmitters in vivo with carbon microelectrodes.[11−17] Third, quinone redox reactions are very sensitive to the condition of the electrode surface, on both metal[5−8] and carbon electrodes.[18−19] Electrochemical anodization dramatically increases dopamine (DA) adsorption and electron-transfer rates,[3,17,19−21] an effect often attributed to electrostatic effects or catalysis of proton-transfer reactions. Surface effects on quinone electron transfer have been exploited in bioanalytical applications, including both the rejection of anionic interferences by the creation of an anionic surface and the preconcentration of catecholamines by adsorption preceding voltammetry at fast scan rates.[19] Adsorption of catecholamines to either an anionic film or the carbon surface itself is critical to successful electroanalysis in vivo. Chemisorption of hydroquinones to clean Pt surfaces has been examined extensively,[5,6,8] but adsorption

---

* Corresponding author: (Tel) 614-292-2021; (Fax) 614-292−1685; (e-mail) mccreery.2@osu.edu.

(1) Chambers, J. Q. In *The Chemistry of Quinonoid Compounds;* Patai, S., Rappaport, Z., Eds.; Wiley and Sons: New York, 1988; Vol. II, p 719.

(2) Vetter, K. J. *Z. Elektrochem.* **1952**, *56*, 797.

(3) Cabaniss, G. E.; Diamantis, A. A.; Murphy, W. R.; Linton, R. W.; Meyer, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 1845.

(4) Deakin, M. R.; Wightman, R. M. *J. Electroanal. Chem.* **1986**, *206*, 167.

(5) Soriaga, M. P.; Hubbard, A. T. *J. Am. Chem. Soc.* **1982**, *104*, 2735.

(6) Soriaga, M. P.; Wilson, P. H.; Hubbard, A. T.; Benton, C. S. *J. Electroanal. Chem.* **1984**, *142*, 317.

(7) Laviron, E. *J. Electroanal. Chem.* **1984**, *164*, 213.

(8) Temesghen, W.; Jeng, J.-J.; Carrasquillo, A., Jr.; Soriaga, M. P.; *Langmuir* **1994**, *10*, 3929.

(9) Allred, C. A.; McCreery, R. L. *Anal. Chem.* **1992**, *64*, 448.

(10) Laviron, E. *J. Electroanal. Chem.* **1983**, *146*, 15.

(11) Boulton, A. A.; Baker, G. B.; Adams, R. N., Eds. *Voltammetric Methods on Brain systems*; Humana Press: Totona NJ, 1995.

(12) Ewing, A. G.; Strein, T.; Lau, M. *Acc. Chem. Res.* **1992**, *25*, 440.

(13) Budygin, E.; Gainetdinov, R. R.; Kilpatrick, M. R.; Rayevsky, P. Männistö, K.; Wightman, R. M. *Eur. J. Pharmacol.* **1999**, *370*, 125.

(14) Garris, P.; Kilpatrick, M. R.; Bunin, M.; Michael, D. J.; Walker, Q. D.; Wightman, R. M. *Nature (London)* **1999**, *398*, 67.

(15) Michael, D.; Travis, E. R.; Wightman, R. M. *Anal. Chem.* **1998**, *70*, 586A−592A.

(16) Clark, R. A.; Zerby, S.; Ewing, A. G. Electrochemistry In Neuronal Microenvironments. In *Electroanalytical Chemistry*; Bard, A. J., Rubinstein, I., Eds.; Marcel Dekker: New York, 1998; pp 227−294.

(17) Adams, R. N. *Prog. Neurobiol. (NY)* **1990**, *35*, 297.

(18) McCreery, R. L. Carbon Electrodes: Structural Effects on Electron-Transfer Kinetics. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Dekker: New York, 1991; Vol. 17, pp 221−374.

(19) McCreery, R. L. Carbon Electrode Surface Chemistry: Optimization of Bioanalytical Performance. In *Voltammetric Methods in Brain Systems*; Boulton, A. A., Baker, G. B., Adams, R. N., Eds.; Humana Press: Totowa, NJ, 1995; pp 1−26.

(20) Gonon, F.; Buda, M.; Cespuglio, R.; Jouvet, M.; Pujol, J.-F. *Nature (London)* **1980**, *286*, 902.

(21) Bielby, A.; Carlsson, A. *J. Electroanal. Chem.* **1988**, *248*, 283.

to carbon paste has not been reported. Adsorption to glassy carbon is relatively weak[9,23] and appears to involve physisorption.

The elementary steps of quinone/hydroquinone electron transfer have been described for platinum[2,7] and carbon paste electrodes,[4,22] and in these cases the electrode may be prepared with adequate reproducibility. The "scheme of squares" applies to hydroquinone and catechol oxidation on Pt and carbon paste surfaces, with the order of proton and electron transfer depending on pH. For the case of dopamine oxidation on carbon paste at pH 7, the order was concluded to be H^+, e^-, H^+, e^- to produce the orthoquinone.[4,22] Unfortunately, these conclusions are difficult to generalize to the broad literature on catechol redox reactions because of the variation in carbon surface pretreatment and condition. For example, vacuum heat treatment (VHT) of GC yields a clean surface with a low O/C ratio, while anodization leads to a multilayer oxide film with a high O/C ratio.[18,19] However, DA oxidation kinetics are fast on both VHT and anodized surfaces, raising the question of whether surface oxides are important to electrode kinetics. Even when a redox mechanism is established following a given carbon surface preparation, it is risky to assume that the same mechanism applies after a different preparation or for a different carbon-electrode material.

Our approach to this problem has been to prepare and characterize reproducible carbon surfaces, particularly those derived from glassy carbon. Through well-defined cleaning and modification procedures, GC surfaces with reproducible kinetic behavior may be fabricated and spectroscopically characterized. The approach was used successfully to demonstrate that several outer-sphere redox systems (e.g., $Ru(NH_3)_6^{+3/+2}$, methyl viologen, chlorpromazine) are fairly insensitive to surface modifications and electron transfer can occur via electron tunneling through an organic monolayer chemisorbed on GC.[24-26] In contrast, redox systems such as $Fe^{3+/2+}$, dioxygen reduction, and NADH oxidation are critically dependent on interaction with specific surface sites.[27-30]

In a previous report,[23] we assessed the effects of surface modifications of glassy carbon electrodes on catechol and hydroquinone electrochemistry. Coverage of the electrode surface with a chemisorbed monolayer was found to severely or completely inhibit catechol electron-transfer activity, in contrast to the outer-sphere systems. Also, catechol adsorption was found to accompany fast electron transfer on solvent-cleaned and VHT treated surfaces. The results indicate that adsorption of the catechol to the electrode surface is necessary for fast electron transfer and that the inhibition of the electron transfer at monolayer covered surfaces is caused by prevention of catechol adsorption. Electron tunneling through an inert chemisorbed monolayer does not occur for the catechols, leading to the requirement for adsorption. In this report, we investigate
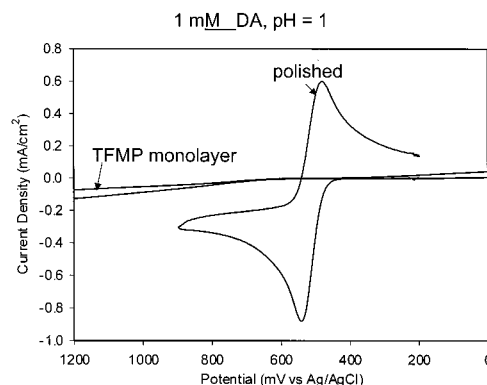
Figure 1. Voltammograms of dopamine in 0.1 M H_2SO_4 on polished GC and on GC modified with a monolayer of covalently bonded trifluoromethylphenyl groups. The F/C ratio from XPS for the TFMP surface was 0.25. Scan rate, 0.2 V/s.

the nature of the adsorption between the catechols and the electrode surface and its importance to the electron-transfer rate.

Experimental Section (Additional Details Are Provided in Supporting Information)

GC electrodes were polished by established procedures[24,25,27] using alumina slurries in "Nanopure" water (Barnstead Nanopure System, Dubuqu, IA). Unless indicated otherwise, electrodes underwent a solvent-cleaning step,[31] either with reagent-grade pyridine or with 2-propanol containing activated carbon (IPA/AC). Catechol and quinone solutions were prepared either in 0.1 M H_2SO_4 or 0.1 M PBS. Where noted, 0.1 M D_2SO_4 in 99% D_2O was substituted for 0.1 M H_2SO_4 in H_2O. Dopamine (DA), hydroquinone, and duroquinone (DUQ) were used as received, and 4-methylcatechol (4MC) was recrystallized from toluene. *p*-Nitrobenzenediazonium tetrafluorobate, α,α,α-trifluoro-methylbenzenediazonium tetrafluorobate and 4-diazonium benzoic acid tetrafluoroborate were prepared according to Dunker et al.,[32] and reacted with GC surfaces as described previously,[33,34] using three voltammetric scans between 0 and -1.4 V vs Ag/Ag^+ at 200 mV/s.

AQDS, DUQ and 4MC were "preadsorbed" from approximately 1 mM solution, then rinsed thoroughly and transferred to a catechol solution for voltammetry. In some cases, both AQDS and the catechol were present in the bulk voltammetry solution. Details appear in the Supporting Information.

Cyclic voltammetry was carried out using a BAS 100/W electrochemical workstation (Bioanalytical Systems, Inc., West Lafayette, IN). Each voltammogram was recorded on a freshly prepared surface unless otherwise noted. Survey and regional XPS spectra were acquired with a VG Scientific Escalab MKII spectrometer with a Mg anode, and all atomic ratios were corrected for the instrumental sensitivity factor.

Results

We reported previously on catechol and hydroquinone electron-transfer kinetics on glassy carbon surfaces.[23] From that work, we found that a chemisorbed monolayer severely inhibits catechol oxidation and, in case of DA, oxidation was not observable. An example is shown in Figure 1 for the case of a trifluoromethylphenyl (TFMP) monolayer on GC. The polished GC surface exhibits rapid electron-transfer kinetics for DA oxidation, while the modified surface is inert. The same monolayer has minor effects on ET to outer-sphere redox systems such as $Ru(NH_3)_6^{+3/+2}$, due to electron tunneling through the organic monolayer.[23] When a polished GC surface

(22) Deakin, M.; Kovach, P.; Stutts, K.; Wightman, R. M. *Anal. Chem.* **1986**, *58*, 1474.

(23) DuVall, S. H.; McCreery, R. L. *Anal. Chem.* **1999**, *71*, 4594.

(24) Chen, P.; McCreery, R. L. *Anal. Chem.* **1996**, *68*, 3958.

(25) Chen, P.; Fryling, M. A.; McCreery, R. L. *Anal. Chem.* **1995**, *67*, 3115.

(26) Yang, Hseuh-Hui; McCreery, R. L. *Anal. Chem.* **1999**, *71*, 4081.

(27) McCreery, R. L. In *Laboratory Techniques in Electroanalytical Chemistry*, 2nd ed.; Kissenger, P. T., Heineman, W. R., Eds.; Dekker: New York; 1996; Chapter 10.

(28) McDermott C. A.; Kneten K. R.; McCreery R. L. *J. Electrochem. Soc.* **1993**, *140*, 2593.

(29) McCreery, R. L.; Cline, K. K.; McDermott, C. A.; McDermott, M. T. *Colloids Surf.* **1994**, *93*, 211.
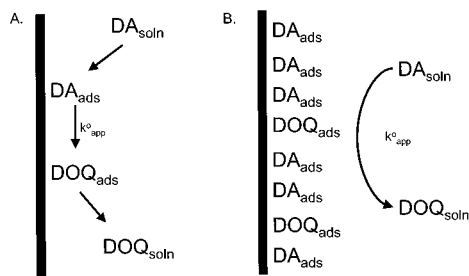
(30) Yang, H.-H.; McCreery, R. L. *J. Electrochem. Soc.*, in press.

(31) Ranganathan, S.; Kuo, T.-C.; McCreery, R. L. *Anal. Chem.* **1999**, *71*, 3574.

(32) Dunker, M. F. W.; Strarkety, E. B.; Jenkins, G. L. *J. Am. Chem. Soc.* **1936**, *58*, 2308.

(33) Allongue, P.; Delamar, M.; Deshat, B.; Fagebaume, O.; Hitmi, R.; Pinson, J.; Saveant, J. M. *J. Am. Chem. Soc.* **1997**, *119*, 201.

(34) Liu, Y.-C., McCreery R. L. *J. Am. Chem. Soc.* **1995**, *117*, 11254.

Figure 2. Schematic models for adsorption-dependent electron transfer. (A) requires an adsorption/electron transfer/desorption sequence, while (B) involves electron transfer through a static adsorbed DA/DOQ layer.
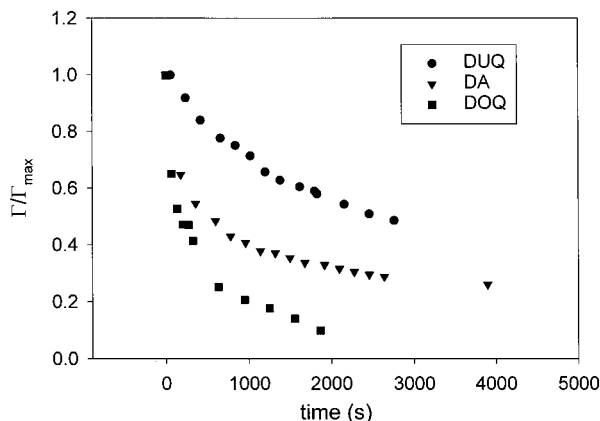
Figure 3. Coverage of dopamine (DA), duroquinone (DUQ), and dopamine orthoquinone (DOQ) determined voltammetrically as a function of time after immersion of a preadsorbed GC surface in 0.1 M H$_2$SO$_4$. The rest potential between voltammograms was 0 V for DA, -0.2 V for DUQ, and 0.8 V for DOQ.

Figure 4. Voltammetry of dopamine (0.2 V/s) in 0.1 M H$_2$SO$_4$, on solvent-cleaned (IPA/AC) and MB or DUQ modified surfaces. DUQ and MB were adsorbed to a IPA/AC surface, and then the electrode was transferred into DA solution.

is cleaned with a suspension of activated carbon in 2-propanol, both DA adsorption and ET rates increase. We concluded, from these and other observations, that adsorption is essential for rapid electron transfer to the catechol/orthoquinone redox center for DA and several other catechols, as well as hydroquinone. Understanding the relationship between adsorption and ET kinetics is the main objective of the current work.

A fairly obvious possibility for catalysis based on catechol adsorption is a multistep mechanism involving an adsorbed intermediate. If electron transfer between the GC and an adsorbed catechol (or quinone) is fast, then oxidation of a solution species might proceed via adsorption followed by ET and then desorption of the product (Figure 2A). For this mechanism to be viable, however, the desorption rate of the product must be fast enough to support the required flux of reactant adsorbing to the GC surface. Otherwise, adsorption sites will saturate with the product and the current will approach zero.

The desorption rate from a GC electrode surface was tracked by preadsorbing DA onto IPA/AC treated GC for 10 min from a 1 mM solution of DA in 0.1 M H$_2$SO$_4$. The electrode was removed from the DA solution, rinsed thoroughly, and placed in a degassed solution of 0.1 M H$_2$SO$_4$. Surface DA coverage was determined from cyclic voltammograms taken at time intervals ranging from 30 s to 5 min. (Figure 3). The same procedure was used to determine desorption of dopamine *o*-quinone (DOQ) from the electrode surface, except that the rest potential between voltammograms was the positive of $E_{1/2}$ for dopamine. This ensured that DOQ desorption was being monitored, not DA desorption. Initial rates of desorption were determined from each plot and found to be 0.3 pmol cm^{-2} s^{-1} for both DA and DOQ. The rate required for the observed peak
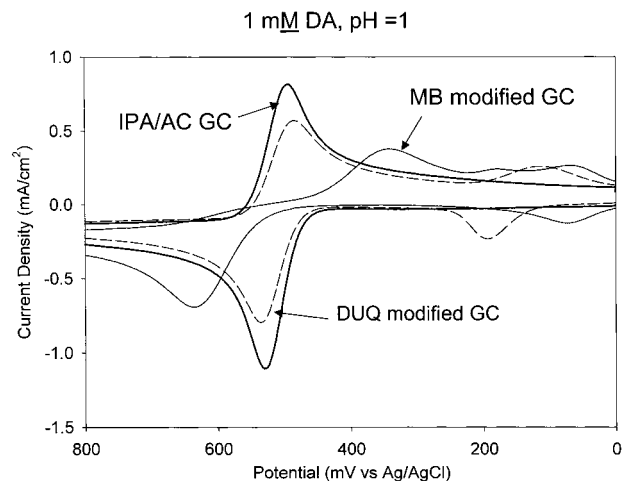
current of a voltammogram of 1 mM DA in 0.1 M H$_2$SO$_4$ on IPA/AC treated GC is 4000 pmol cm^{-2} s^{-1} for $i_p = 750$ μA/cm^2 at 0.20 V/s. Therefore, the desorption rate of either DA or DOQ from the GC surface is 4 orders of magnitude lower than that required to support the observed current. Stated differently, inhibition of an adsorption/desorption mechanism such as that shown in Figure 2A by an organic monolayer cannot explain the dramatic effect shown in Figure 1.

The results thus far indicate that electron transfer can occur rapidly on an adsorbed catechol layer, but not on nitrophenyl or TFMP monolayers. The adsorbed catechol layer must be acting as an electrocatalyst, greatly increasing the electron-transfer rate compared with a nitrophenyl, TFMP, or methylene blue modified surface. The self-catalytic effect may be caused by redox mediation by adsorbed catechol or by some other interaction between adsorbed and solution species. To investigate these possibilities, a variety of physisorbed and chemisorbed monolayers were investigated for their effects on catechol kinetics.

Duroquinone (DUQ) has an $E_{1/2}$ of 152 $\pm$ 2 mV($N = 4$) in 0.1 M H$_2$SO$_4$, and DUQ coverage may be monitored simultaneously with DA voltammetry. The desorption rate of DUQ from GC is shown in Figure 3, yielding a rate for DUQ in blank electrolyte of 0.2 pmol cm^{-2} s^{-1}. Figure 4 shows DA voltammetry on IPA/AC treated GC and on GC modified by MB or DUQ adsorption. ΔE_p for DA on MB modified GC increases by 280 mV compared with the IPA/AC surface, which indicates a decrease in k°_{obs} of $\sim$3 orders of magnitude. DUQ modified GC exhibits a slight increase in ΔE_p for DA and a decrease in i_p. Theoretical coverage of DUQ on a flat surface was calculated from its molecular area to be 199 pmol/cm^2 for flat orientation and 422 pmol/cm^2 for edgewise adsorption on a flat surface.[5] The observed values of 433$-$527 pmol/cm^2 are higher than those calculated geometrically for the expected flat orientation, presumably due to the roughness factor of polished GC (1.5$-$2.5).[35] Voltammetry of DA in the 10$-$100 μm range shows that DA adsorption is prominent on the IPA/AC surface, but is suppressed on DUQ pretreated GC. Semi-integration of these voltammograms confirmed that DA adsorption was prevented by preadsorption with DUQ[36] (results available in Supporting

(35) Pontikos, N. M.; McCreery, R. L. *J. Electroanal. Chem.* **1992**, *324*, 229.

(36) Bowling, R.; McCreery, R. L. *Anal. Chem.* **1988**, *60*, 605.

Table 1.   Observed ΔE_p and $E_{1/2}$ for Catechol Derivatives on Modified Surfaces (1 mM, except where otherwise noted. 200 mV/s)

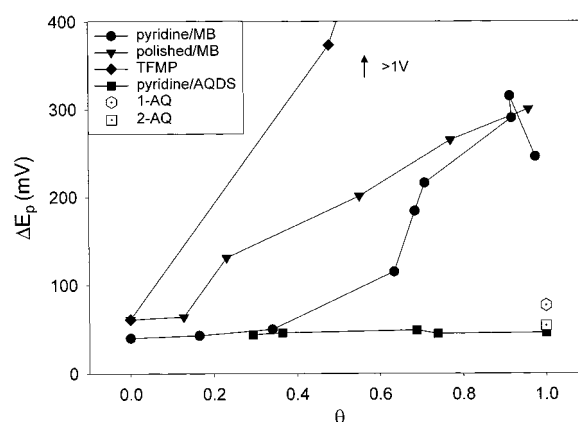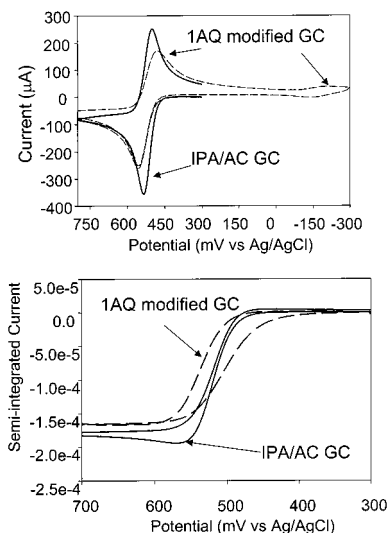|	$E_{1/2,}$ [a] mV	DA pH = 1	DA pH = 7	4MC pH = 1	4MC pH = 7	DOPAC pH = 1	DOPAC pH = 7	DOPEG[b] pH = 1	DOPEG[b] pH = 7
				glassy carbon:					
polished		$61 \pm 8^c[61 \pm 7]^d$	67 ± 10	62 ± 7	85 ± 18	61 ± 8	115 ± 6	47 ± 4	65 ± 3
IPA/AC		$36 \pm 6 [39 \pm 2]$	41 ± 5	39 ± 1	59 ± 4	40 ± 2	71 ± 5	37 ± 1	41 ± 4
pyridine		43 ± 2	48 ± 3	47 ± 2	53	42 ± 4	75 ± 9	40 ± 4	72 ± 2
				physisorbed monolayers:					
MB	76	315 ± 7	193 ± 17^e	256 ± 4^e	210 ± 11^e	208 ± 8^e	274 ± 6^e	267 ± 18^e	253 ± 3^e
DUQ	152 ± 2	$51 \pm 6 [71 \pm 3]^d$	47 ± 8	48 ± 6	84 ± 1	64 ± 7	83	43 ± 2	76
AQDS	-117	47 ± 2	69	41 ± 5	98 ± 7	47 ± 4	213 ± 6	57 ± 2	103 ± 10
4MC	465	38 ± 4							
				chemisorbed monolayers:					
NP		>1000	>1000	>1000	468 ± 6	>650	>1000	>1000	>800
TFMP		>1000	>1000	>1000	>1000	>1000	>800		
COOH		$439 [463]^d$	114	197	172	262 ± 2	530	262	264
1-AQ	-151	77 ± 2							
2-AQ	-182	54 ± 5			92 ± 4	90 ± 3			

[a] $(E_p{}^a + E_p{}^c)/2$ for adsorbed species (pH = 1). [b] DOPEG concentration was 0.4 mM. [c] Values shown are mean ± standard deviation for at least three different electrode surfaces. [d] Values in brackets were observed in 0.1 M D_2SO_4/D_2O. [e] Residual catechol adsorption observed.
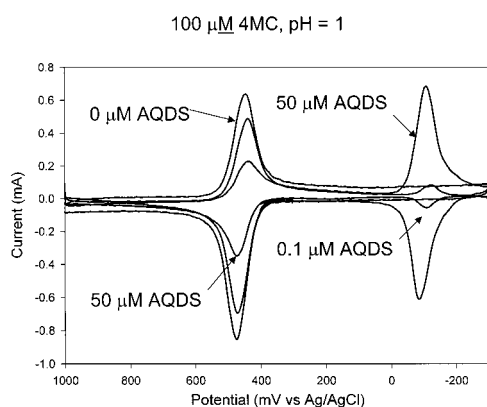
Figure 5. 4-methyl catechol voltammetry in the presence of varying concentrations of AQDS. 0.1 M H_2SO_4, 0.2 V/s. Bulk 4MC concentration was 0.1 mM.

Figure 6. Effect of surface coverage of physisorbed MB, AQDS, and chemisorbed TFMP and AQ on ΔE_p for DA, 0.1 M H_2SO_4, 0.2 V/s. Coverage ($\theta = \Gamma/\Gamma_{sat}$) determined from voltammetry for MB, AQDS, and AQ or the XPS F/C ratio for TFMP. "Pyridine" refers to a solvent pretreatment in warm pyridine.[23]

Information). Similar behavior was observed for DA voltammetry acquired in solutions containing AQDS, shown for the case of 4MC in Figure 5. As the bulk AQDS concentration increases, 4MC is displaced from the electrode surface and the 4MC peak changes from primarily an adsorption feature to primarily a diffusion. A plot of AQDS vs 4MC determined from voltammetric peak areas, similar to those in Figure 5, shows a linear, inverse correlation (Supporting Information) indicating competitive adsorption. The effects for MB, DUQ, and AQDS on catechol voltammetry are summarized in Table 1 and in Figure 6, which shows kinetic effects as a function of coverage. The important observation about the physisorbed monolayers is that the adsorbed quinones can suppress catechol adsorption but have minor effects on catechol ET kinetics.

To ensure that the species in solution does not displace the adsorbed quinone, 9,10-anthraquinone was chemisorbed to GC by reduction of the corresponding diazonium salt.[33,34] Two different salts were used, providing two different points of attachment, (designated 1-AQ and 2-AQ). Kuo was able to observe 1-AQ chemisorbed to GC with Raman spectroscopy.[37] Coverage of the surface AQ species was monitored by integration of the voltammetric reduction peak in 0.1 M H_2SO_4. Coverage of 1-AQ was determined to be 388 ± 24 pmol cm^{-2} ($N = 3$), and 2-AQ coverage was 321 ± 76 pmol cm^{-2} ($N =$

Figure 7. Voltammograms and semi-integrals of DA (0.1 M H_2SO_4, 0.2 V/s) on GC modified with chemisorbed 1-anthraquinone.

5). Figure 7 shows the voltammetry and semi-integral of DA on IPA/AC treated GC and on GC modified with covently bonded 1-AQ.

Finally, electrostatic effects on DA kinetics were considered, by preparing a GC surface modified with phenylcarboxylate

(37) Kuo, T.-C. Raman Spectroscopy and Electrochemistry of Modified Carbon Surfaces. Ph.D. Dissertation, The Ohio State University, Columbus, OH, 1999.

groups via reduction of 4-diazonium benzoic acid.[33,38] Without a voltammetric or XPS marker, the ϕ-COOH coverage was not assessed quantitatively, but the voltammetry observed during reduction of the diazonium salt was similar to that with NP and TFMP variants. Table 1 includes results from the ϕ-COOH modified GC surface at pH 1, where the carboxylate is protonated, and at pH 7, where the surface is anionic. The corresponding voltammograms are available as Supporting Information.

Discussion

Several conclusions are available from the results, which bear directly on the catechol ET mechanism on glassy carbon electrodes. First, electron transfer through an inert film such as chemisorbed nitrophenyl or physisorbed methylene blue is very slow, indicating that tunneling through such layers is inefficient. Unlike methyl viologen, $Ru(NH_3)_6^{+3/+2}$, etc.,[24,26] the catechols must have a high reorganization energy which impedes outer-sphere electron transfer. Second, an adsorption/ET/desorption pathway is too slow to explain the observed voltammetric currents, due to the slow desorption kinetics of reduced or oxidized catechol. Third, electron transfer occurs through an adsorbed quinone film, whether the quinone is physisorbed (AQDS, DUQ) or chemisorbed (1 or 2-AQ). Although the films examined here were in either the oxidized or mixed redox state during electron transfer, the identity of the adsorbed quinone had little effect on the ET rate. Fourth, variation of the initial surface O/C ratio from about 12% to less than 4% had little effect on the observed ET kinetics. Fifth, similar kinetic effects of surface modification were observed for neutral, cationic, and anionic catechols. However, electrostatic attraction or repulsion between the modified surface and the solution redox system did influence the observed ΔE_p (e.g., the ϕ-COOH surface at pH 1 and 7). It should be emphasized that fast electron transfer is decoupled from observable DA adsorption in the case of the DUQ or AQ modified surfaces. Figures 5 and 7 show that fast electron transfer may occur when catechol adsorption is suppressed, provided the adsorbate is also a quinone. The catechol in solution may be self-catalytic, with its own adsorption creating the catalytic layer. On the other hand, observable catechol adsorption is not required if a suitable surface catalyst (e.g., DUQ, AQ, etc.) is present. A brief interaction of a solution-phase catechol with a surface quinone to form an intermediate is certainly possible, but no detectable surface excess was observed for catechols on the DUQ, AQDS, or 1-AQ modified surfaces.

A semiquantitative estimate of the changes in electron-transfer rates indicated by observed ΔEp values may be gained from a simulation of the "scheme of squares" mechanism using commercial software (Digisim, Bioanalytical Systems, West Lafayette, Indiana). Wightman and co-workers concluded that catechol oxidation at neutral pH followed an HeHe mechanism on carbon paste, and several microscopic rate constants for the scheme of squares were calculated[4,22,39]. Using a similar approach combined with thermodynamic data, we determined $E°'_{Q/HQ} = 0.011$ V and $E°'_{HQ/H2Q} = 0.297$ V at pH 7, both vs Ag/AgCl. Voltammograms for DA oxidation were simulated using these $E°'$ values, a pH of 7, transfer coefficients equal to 0.5, and diffusion coefficients equal to 6×10^{-6} cm^2/s for a range of $k°$ values. The two $k°$ values for the HeHe mechanism

cannot be determined independently from available results, but a useful estimate of their effects on observed ΔE_p can be made by assuming $k°_{Q/QH} = k°_{QH/QH2}$ and that protonations remain in equilibrium throughout the process.[7,22,39] For the IPA/AC treated surface, the best fit of simulated to observed ΔE_p for DA at pH 7 occurs when $k°_{Q/QH} = k°_{QH/QH2} = 0.36 \pm 0.06$ cm/s (mean and standard deviation for fits to three experimental voltam-mograms). This is likely to be an overestimate due to the effect of DA adsorption. For the duroquinone modification, where DA adsorption is negligible, ΔE_p implies a $k°$ of 0.24 ± 0.05 cm/s. For MB and TFMP modified GC, the simulation yields $k° = 0.024 \pm 0.002$ and $< 1 \times 10^{-8}$ cm/s, respectively. These simulations necessarily involve some assumptions, but they do indicate that duroquinone and other adsorbed quinones can block DA adsorption while having minor effects on electron-transfer rate, while other monolayers reduce the ET rate by a factor of 10 (MB) or as much as a factor of 10^7 (TFMP). Very similar trends were observed for 4MC on modified surfaces, and 4MC voltammograms are shown in the Supporting Information.

A possibility which might explain these observations is redox mediation, as described for several modified electrodes used to oxidize biological redox systems. The adsorbed quinone may undergo fast electron transfer with the GC, then a redox cross reaction between the adsorbed quinone and a catechol in solution might result in ET to solution species. Such mechanisms have been firmly established for a variety of cases, including porphyrin catalysis of O_2 reduction[40-43] and catalysis of NADH oxidation by adsorbed quinones.[44,45] However, redox mediation is not a viable explanation for the present results for several reasons. First, the voltammetric waves should occur near the mediator $E°$, not the solution component, if a redox mediation mechanism is active. Table 1 shows that adsorbates with a range of $E°$ values exhibit comparable catalysis, with the catechol redox wave appearing at a constant potential. Second, several adsorbates studied would be able to catalyze DA oxidation by a redox mediation route, but not DOQ reduction. For example, AQ and DUQ remain oxidized during DA oxidation and reduction. Oxidized DUQ could conceivably oxidize solution DA (although this reaction is thermodynamically uphill), but oxidized DUQ cannot reduce solution DOQ. Furthermore, a very asymmetric wave would be expected for these cases. It is possible that redox mediation occurs for DA self-catalysis, since both adsorbed DA and DOQ would coexist on the GC during voltammetry of DA in solution. However, redox mediation is not operative for the AQ and DUQ cases, and a different mechanism may apply to all the adsorbed catalysts studied.

An alternative mechanism to redox mediation must support catalysis by an adsorbed quinone monolayer, without a change in adsorbate redox state. Classical studies have identified interactions between quinones and hydroquinones, particularly quinhydrone, in which a quinone and hydroquinone bind to form a symmetric complex of two semiquinones attached face to face by hydrogen bonding. More recently, "proton-coupled electron transfer" has been reported,[3,46,47] in which electron and proton transfer occur synchronously. For an electrochemically oxidized

(38) Downard, A. J.; Roddick, A. D.; Bond, A. M. *Anal. Chim. Acta.* **1995**, *717*, 303−310.

(39) Kawagoe, K.; Garris, P.; Wightman, R. M. *J. Electroanal. Chem.* **1993**, *359*, 193.

(40) Shi, C.; Anson F. *Inorg. Chem.* **1990**, *29*, 4298−4305.

(41) Buttry, D.; Anson, F. *J. Am. Chem. Soc.* **1984**, *106*, 59.

(42) Forshey, P.; Kuwana, T. *Inorg. Chem.* **1983**, *22*, 699.

(43) Hossian, M. S.; Tryk, D.; Yeager, E. *Electrochim. Acta* **1989**, *34*, 1733−1737.

(44) Jaegfeldt, H.; Kuwana, T.; Johansson, G. *J. Am. Chem. Soc.* **1983**, *105*, 1805.

(45) Tse, D.; Kuwana, T. *Anal. Chem.* **1978**, *50*, 1315.

(46) Huynh, M. H.; Meyer, T.; White, P. *J. Am. Chem. Soc.* **1999**, *121*, 4530.

(47) Trammell, S. A.; Wimbish, J. C.; Odebel, F.; Gallagher, L. A.; Narula, P. M.; Meyer, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 13248.

GC surface, it has been proposed that surface oxides assist proton transfer for redox processes in which both electron and proton transfer are involved. For this mechanism, H/D kinetic isotope effects were observed for catechol oxidation, H_2O_2 oxidation, and electron transfer to metal complexes.[3] For catechol oxidation below pH 2, the order of electron and proton transfers has been identified as eHeH.[4] It is conceivable that the surface quinone layer could interact with the solution-phase redox system to assist proton transfer, in which case an H/D isotope effect would be expected. Table 1 includes a few observations for catechol oxidation in 0.1 M D_2SO_4/D_2O, shown in brackets. For the DUQ and ϕ-COOH modified surfaces, there are small increases in ΔE_p, implying a slower rate in D_2O compared with that in H_2O. The magnitude of the H/D effect is difficult to assess without knowing the detailed mechanism, but it appears to be smaller than that reported for systems undergoing proton-coupled electron transfer.[3,46,47] A related possibility is hydrogen bonding between the catechol and surface quinone, which may affect the activation barrier for electron transfer. For example, the first step in the eHeH mechanism yields a high-energy H_2Q^+ species. This process may be accelerated if the catechol OH group could hydrogen bond to a surface carboxyl group on either an adsorbed quinone or a surface functional group.

A remaining issue is whether electrostatics play a significant role in catechol kinetics on glassy carbon. DA has faster kinetics and increased adsorption on highly oxidized glassy carbon, which contains many anionic sites. Downard et al.[38] found that ΔE_p for DA on a surface that had been modified with phenylacetate groups decreased to 245 mV, compared with 465 mV on polished GC (PBS, 0.1 v/s). The increased ET rate was attributed to attraction between DA and anionic surface carboxylates. The ϕ-COOH modified surface was examined here with the results listed in Table 1. The absence of a useful XPS tag or voltammetric wave for the ϕ-COOH surface prevented an accurate estimate of surface coverage, so a compact monolayer was not established for this case. The COOH modification increased ΔE_p for all redox systems examined, but did not have as dramatic an effect as that observed for NP or TFMP monolayers. The reason for the smaller inhibition by the COOH modification is not clear, but may result from incomplete surface coverage. For the neutral solution species (DOPEG and 4MC), deprotonation of the surface carboxylate by changing the pH from 1 to 7 had little effect on ΔE_p. For cationic DA, however, the deprotonated surface exhibited a smaller ΔE_p (114 mV) than the neutral surface (439 mV). Conversely, DOPAC at pH 1 (where both surface and redox couple are neutral) exhibits a smaller ΔE_p than at pH 7 (where both surface and redox system are anionic). The observation indicates that electrostatic effects can modulate the observed rate but they cannot be the only factor. Blocking the surface with a neutral inert monolayer can completely suppress ET, but electrostatic effects can increase or decrease observed kinetics at a partially active surface. This conclusion is consistent with the Frumkin effects reported for inorganic redox systems on anionic GC surfaces.[48] For very reactive GC surfaces (IPA/AC or pyridine treated), electrostatic effects are small or not observable at all for the catechols.

The fact that deprotonation of a surface carboxylic acid has no effect on the ΔE_p for the neutral redox systems (4MC and DOPEG) is mechanistically significant. We conclude that the COO^- group is not catalytic for 4MC and DOPEG, since a large change in its surface concentration from pH 1 to 7 has no

apparent effect on observed kinetics. For DA and deprotonated DOPAC, the effect on ΔE_p is in the direction expected for a Frumkin effect caused by local ionic attraction (or repulsion) between the surface and the analyte. Therefore, the catalysis observed for physi- or chemisorbed quinones is not an electrostatic effect, since it is present for neutral monolayers and/or a neutral redox couple in solution.

The consequences of the current results bear directly on the electrochemical behavior of dopamine and other catechols on a range of carbon electrode surfaces. Many of the activation procedures in common use may be explained in terms of self-catalysis between an adsorbed and a solution quinone redox system. A clean GC electrode resulting from laser activation,[49] fracturing in solution,[9] or solvent cleaning[31] yields fast electron transfer because DA adsorption is increased over that on a polished surface. Highly ordered pyrolytic graphite (HOPG) is particularly inactive toward DA oxidation because adsorption is weak or nonexistent. When the HOPG lattice is damaged by oxidation or laser activation,[50] the electron transfer rate increases dramatically as adsorption and electron-transfer rate sites are generated. Anodization of GC or carbon fibers increases both adsorption and electron-transfer rates. In this case, catalysis may occur at either the adsorbed catechol or oxides on the carbon surface. As noted earlier, oxygen-containing functional groups do not appear to be required, provided the catechol can adsorb to provide a catalytic site. However, it is possible that surface oxides are catalytic, in parallel with adsorbed catechols. Finally, the pronounced sensitivity of DA kinetics to competitive adsorption by intentional or adventitious impurities[9,48] is due to prevention of catechol adsorption and associated catalysis.

In summary, electron transfer between catechols and GC electrodes is catalyzed by a layer of adsorbed quinones. The adsorbed catalyst may be a physisorbed quinone, the catechol itself, or a chemisorbed quinone. The faster kinetics observed for catechols on electrochemically oxidized GC is due to an increase in DA adsorption or an increase in surface-oxide level or both. The observed catalysis is not consistent with either a redox mediation mechanism, or with a stepwise process involving catechol adsorption, electron transfer, and desorption. A likely candidate for the catalytic step is hydrogen bonding between a surface quinone oxygen and the catechol. Such interactions may catalyze one or more of the steps in the scheme of squares, thus accelerating the overall redox process.

Supporting Information Available: Voltammograms of DA on IPA/AC and DUQ modified GC; voltammograms of DA on polished, NP, and ϕ-COOH modified GC; a graph of competitive adsorption between 4MC and AQDS; a table of rate constants and simulated voltammograms; and additional experimental details are given. This material is available free of charge via the Internet at http://pubs.acs.org.

JA000227U

---

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

(49) Rice, R. J.; Pontikos, N.; McCreery, R. L. *J. Am. Chem. Soc.* **1990**, *112*, 4617.

(50) Bowling, R.; Packard, R.; McCreery, R. L. *J. Am. Chem. Soc.* **1989**, *111*, 1217.