

# Effects of Surface Monolayers on the Electron-Transfer Kinetics and Adsorption of Methyl Viologen and Phenothiazine Derivatives on Glassy Carbon Electrodes

Hseuh-Hui Yang and R. L. McCreery\*

Department of Chemistry, The Ohio State University, 100 West 18th Avenue Columbus, OH 43210

Five organic redox systems were examined in aqueous electrolytes on polished and chemically modified glassy carbon (GC), to evaluate the effects of surface structure on the heterogeneous transfer rate constant,  $k^\circ$ . Methyl viologen reduction to its cation radical exhibited a voltammetric peak potential difference which was insensitive to surface modification, with  $k^\circ$  decreasing by only 50% when a chemisorbed monolayer was present. Methylene blue and three other phenothiazines adsorbed to polished GC, but the adsorption was suppressed by surface modification. For all four phenothiazines, chemisorbed or physisorbed monolayers of electroinactive species had minor effects on  $k^\circ$ , with a compact nitrophenyl monolayer decreasing  $k^\circ$  by 50%. This minor change in  $k^\circ$  was accompanied by a major decrease in adsorption, apparently due to inhibition of dipole–dipole or  $\pi$ – $\pi$  interactions between the phenothiazine and GC. Chlorpromazine oxidation to its cation radical was studied in more detail, under conditions where adsorption was suppressed. A plot of the natural log of the observed rate constant vs the monolayer thickness for a variety of chemisorbed monolayers was linear, with a slope of  $-0.22 \text{ \AA}^{-1}$ . The observations are consistent with a through-bond electron-tunneling mechanism for electron transfer to all five redox systems studied. The tunneling constant for CPZ of  $0.22 \text{ \AA}^{-1}$  is between that reported for electron tunneling through conjugated polyene spacers ( $0.14 \text{ \AA}^{-1}$ ) and that reported for phenyl-methylene spacers ( $0.57 \text{ \AA}^{-1}$ ), on the basis of long-range electron transfer in rigid molecules.

Through a variety of efforts from many laboratories, significant progress has been made toward understanding the electrochemical behavior of widely used carbon electrodes.<sup>1–7</sup> Since  $\text{sp}^2$  carbon surfaces are difficult to prepare reproducibly and are prone to

degradation via oxidation and impurity adsorption, our understanding of the behavior of carbon electrodes has lagged that of metal electrodes, particularly mercury ones. This situation improved dramatically after more attention was paid to surface preparation and the number of uncontrolled surface variables was reduced. In particular, several landmarks indicating reproducible performance of  $\text{sp}^2$  carbon electrodes, mainly glassy carbon (GC), have been achieved:

1. Determination of the rapid heterogeneous electron-transfer rate constants ( $k^\circ$ ), for outer-sphere systems (e.g.,  $\text{Ru}(\text{NH}_3)_6^{+3/+2}$   $k^\circ > 0.2 \text{ cm/s}$ ),<sup>8,9</sup> comparable to those observed on Au and Pt.<sup>10</sup>
2. Preparation of low-oxide ( $\text{O/C} < 2\%$ ) carbon surfaces which retain their low oxide levels for at least one month in air.<sup>11,12</sup>
3. Structural characterization of organic monolayers and submonolayers on carbon with Raman spectroscopy.<sup>13–15</sup>
4. Correlation of specific surface sites with electrocatalytic activity for various redox systems, including ascorbic acid, NADH,  $\text{Fe}^{3+/2+}$ , etc.<sup>8,16–19</sup>
5. Systematic classification of redox systems according to their sensitivity to surface chemistry. Classes include outer sphere systems (e.g.,  $\text{Ru}(\text{NH}_3)_6^{+3/+2}$ ,  $\text{Co}(\text{en})_3^{+3/+2}$ , etc.), systems catalyzed by specific surface oxides ( $\text{Fe}_{\text{aq}}^{+3/+2}$ ,  $\text{V}_{\text{aq}}^{+3/+2}$ ,  $\text{Eu}_{\text{aq}}^{+3/+2}$ ), and systems requiring a non-oxide surface site ( $\text{Fe}(\text{CN})_6^{-3/-4}$ , ascorbate).<sup>19,20</sup>

With reproducible carbon electrodes in-hand, it is possible to systematically examine the surface structural factors which control

\* Corresponding author. Tel.: 614-292-2021. Fax: 614-292-1685. E-mail: mcCreery.2@osu.edu.

- (1) McCreery, R. L. Carbon Electrodes: Structural Effects on Electron-Transfer Kinetics. In *Electroanalytical Chemistry*; A. Bard, Ed.; Marcel Dekker: New York, 1991; Vol. 17.
- (2) Kinoshita, K. *Carbon: Electrochemical and Physicochemical Properties*; Wiley: New York, 1988.
- (3) McCreery, R. L.; Cline, K. K.; McDermott, C. A.; McDermott, M. T. *Colloids and Surf.* **1994**, 93, 211.
- (4) Hu, I. F.; Karweik, D. H.; Kuwana, T. *J. Electroanal. Chem.* **1985**, 188, 59.

- (5) Wightman, R. M.; Deakin, M. R.; Kovach, P. M.; Kuhr, P. M.; Stutts, K. J. *J. Electrochem. Soc.* **1984**, 131, 1578.
- (6) Nowall, W. B.; Kuhr, W. G. *Anal. Chem.* **1995**, 67, 3583.
- (7) Xu, J.; Chen, Q.; Swain, G. M. *Anal. Chem.* **1998**, 70, 3146.
- (8) Chen, P.; Fryling, M. A.; McCreery, R. L. *Anal. Chem.* **1995**, 67, 3115.
- (9) Jaworski, R. K.; McCreery, R. L. *J. Electroanal. Chem.* **1994**, 369, 175.
- (10) Iwasita, T.; Schmickler, W.; Schultze, J. W. *Ber. Bunsen-Ges. Phys. Chem.* **1985**, 89, 138.
- (11) Fagan, D. T.; Hu, I. F.; Kuwana, T. *Anal. Chem.* **1985**, 57, 2759.
- (12) Kuo, T.-C.; McCreery, R. L., *Anal. Chem.* **1999**, 71, 1553.
- (13) Kagan, M. R.; McCreery, R. L. *Langmuir* **1995**, 11, 4041.
- (14) Liu, Y.-C.; McCreery, R. L. *J. Am. Chem. Soc.* **1995**, 117, 11254.
- (15) Liu, Y.-C.; McCreery, R. L. *Anal. Chem.* **1997**, 69, 2091.
- (16) McDermott, C. A.; Kneten, K. R.; McCreery, R. L. *J. Electrochem. Soc.* **1993**, 140, 2593.
- (17) Deakin, M.; Stutts, K.; Wightman, M. J. *J. Electroanal. Chem.* **1985**, 182, 113.
- (18) Tse, D. C. S.; Kuwana, T. K. *Anal. Chem.* **1978**, 50, 1315.
- (19) Chen, P.; McCreery, R. L. *Anal. Chem.* **1996**, 68, 3958.
- (20) McCreery, R. L. Electrochemical Behavior of Carbon Surface. In *Interfacial Electrochemistry*; A. Wieckowski, Ed.; Marcel Dekker: N.Y., 1999.

electron transfer reactivity, adsorption, capacitance, etc. In previously reported experiments, we used several electrode modifications to classify a collection of mainly inorganic redox systems according to their sensitivity to surface structure.<sup>19</sup> Outer-sphere systems such as  $\text{Ru}(\text{NH}_3)_6^{+3/+2}$  showed minor kinetic effects of surface modification, even when a compact organic monolayer was chemisorbed to the surface before kinetic measurements. In contrast, rate constants for  $\text{Fe}^{3+/2+}$  and related systems were dramatically affected by surface preparation, due to electrocatalysis by surface carbonyl groups.<sup>8</sup> For these systems, the outer-sphere rate in the absence of carbonyl groups was comparable to that observed on metals, and carbonyl groups increased the observed rate by electrocatalysis.

While a framework relating surface modification to kinetic effects on GC is quite useful for the  $\sim 15$  redox systems classified to date, its generality is unknown. Ascorbic acid was the only organic redox system examined under the same procedure, and organic redox reactions are generally more complex. The current work was undertaken to identify carbon surface structural effects on electron-transfer kinetics for several organic redox systems, some with biological importance. Chlorpromazine, promazine, triflupromazine, methylene blue, and methyl viologen were subjected to the systematic analysis used previously for inorganic redox reactions. The results reveal correlations between redox mechanism and surface effects and provide unexpected new information on the effect of surface structure on reactant adsorption. In addition, the approach addresses the issue of long-range electron transfer between carbon surfaces and organic redox systems in solution.

## EXPERIMENTAL SECTION

**Reagents.** Tetrabutylammonium tetrafluoroborate ( $\text{NBu}_4\text{BF}_4$ ), 50% fluoboric acid, disodium 2,6-anthraquinonedisulfonate (AQDS), methylene blue, 1,4-bis(2-methylstyryl)benzene (BMB), aniline, *p*-toluidine, 4-ethylaniline, 4-(trifluoromethyl)aniline, 4-nitroaniline, 4-aminobiphenyl, and disperse orange 3 (4-nitro, 4'-amino azobenzene) were purchased from Aldrich Chemical Co. and were used as received, except AQDS was recrystallized from water. Chlorpromazine (CPZ), promazine (PMZ), triflupromazine (TPZ), methyl viologen, and sodium nitrite were purchased from Sigma Chemical Company and used as received. Ether and cyclohexane were purchased from J. T. Baker and used as received. Methylene blue and methyl viologen occur as chloride salts and will be referred to herein as  $\text{MB}^+$  and  $\text{MV}^{2+}$  in solution.

**Synthesis of Diazonium Tetrafluoroborate Salts.** Diazonium tetrafluoroborate salts were synthesized according to the procedure described by Starkey et al.<sup>21</sup> One-tenth mole of the corresponding amine precursor was dissolved in 44 mL of 50% fluoboric acid. The solution was placed in an ice bath and stirred with an efficient stirrer, then a cold solution of 0.1 mol of sodium nitrite in 14 mL of water was added dropwise. When the addition was complete, the mixture was stirred for several more minutes and then suction filtered on a sintered-glass filter. The solid diazonium tetrafluoroborate was washed with cold fluoboric acid, ethanol, and ether. The products, with their NMR and mass spectroscopy data, are as follows:

Benzenediazonium fluoborate, NMR ( $d_6$ -DMSO, 250 MHz):  $\delta = 8.00, 8.27, 8.86$  (m, 5H), MS (FAB) calcd for  $\text{C}_6\text{H}_5\text{N}_2$   $m/z$  105.12, found  $m/z$  104.98 ( $\text{M-BF}_4$ )<sup>+</sup>.

4-Methylphenyl fluoborate, NMR ( $d_6$ -DMSO, 250 MHz):  $\delta = 2.59$  (s, 3H), 7.81, 8.56 (d, 4H,  $J = 8.45$  Hz), MS (FAB) calcd for  $\text{C}_7\text{H}_7\text{N}_2$   $m/z$  119.15, found  $m/z$  119.07 ( $\text{M-BF}_4$ )<sup>+</sup>.

Trifluoromethylbenzenediazonium fluoborate, NMR ( $d_6$ -DMSO, 250 MHz):  $\delta = 8.30, 8.92$  (d, 4H,  $J = 8.89$  Hz), MS (FAB) calcd for  $\text{C}_7\text{H}_4\text{N}_2\text{F}_3$   $m/z$  173.12, found  $m/z$  173.05 ( $\text{M-BF}_4$ )<sup>+</sup>.

Ethylbenzenediazonium fluoborate, NMR ( $d_6$ -DMSO, 250 MHz):  $\delta = 1.25$  (t, 3H,  $J = 7.5$  Hz), 2.88 (q, 2H,  $J = 7.5$  Hz), 7.85, 8.58 (d, 4H,  $J = 8.6$  Hz), MS (FAB) calcd for  $\text{C}_8\text{H}_9\text{N}_2$   $m/z$  133.17, found  $m/z$  133.36 ( $\text{M-BF}_4$ )<sup>+</sup>.

Phenylbenzenediazonium fluoborate, NMR ( $d_6$ -DMSO, 250 MHz):  $\delta = 8.33, 8.74$  (d, 4H,  $J = 8.81$  Hz),  $\delta = 7.69$  (m, 5H), MS (FAB) calcd for  $\text{C}_{12}\text{H}_9\text{N}_2$   $m/z$  181.22, found  $m/z$  181.09 ( $\text{M-BF}_4$ )<sup>+</sup>.

Nitroazobenzene diazonium fluoborate, MS(FAB) calcd for  $\text{C}_{12}\text{H}_8\text{N}_5\text{O}$   $m/z$  254.3, found  $m/z$  254.11 ( $\text{M-BF}_4$ )<sup>+</sup>.

**Electrode Materials and Polishing Procedure.** Commercial glassy carbon (GC 20) electrodes from Bioanalytical Systems Inc. (MF2070) were used in this work. Before any modification procedures, electrodes were polished successively in 1  $\mu\text{m}$ , 0.3  $\mu\text{m}$ , and 0.05  $\mu\text{m}$  alumina powder (Buehler) slurries with Nanopure water (Barnstead) on microcloth polishing cloth (Buehler) and subsequently washed and sonicated in Nanopure water for about 10 min. A low-oxide GC surface was prepared by polishing in cyclohexane/alumina slurries instead of Nanopure water/alumina slurries. Cyclohexane was first saturated with argon for 15–20 min. One, 0.3, 0.05  $\mu\text{m}$  alumina slurried with cyclohexane was used successively. Electrodes were polished on bare glass plates and were sonicated in cyclohexane for 3 min and then in Nanopure water for another 10 min.

**Nonspecific Adsorption.** AQDS, methylene blue, and BMB were adsorbed onto glassy carbon according to the previously described procedures.<sup>13,19</sup> GC electrodes preadsorbed with 2,6-AQDS were prepared by placing a polished electrode in 10 mM 2,6-AQDS aqueous solution for 10 min and rinsing with Nanopure water three times. The electrodes were then transferred into electrochemical cells for measurement of voltammetric data. GC electrodes preadsorbed with methylene blue were prepared by dipping a polished electrode in 0.1 mM methylene blue in water for 10 min and rinsing with Nanopure water three times. GC electrodes with preadsorbed BMB were prepared by placing a polished electrode in a 1 mM BMB/acetone solution for 10 min and rinsing with acetone three times.

**Specific Adsorption.** Chemisorption of aryl radicals on GC surfaces was accomplished by the procedure developed by Saveant et al.<sup>22–24</sup> Electrodes were polished successively in 1, 0.3, and 0.05  $\mu\text{m}$  alumina (Buehler) slurries with Nanopure water (Barnstead) on microcloth polishing cloth (Buehler) and subsequently washed and sonicated in Nanopure water for about 10 min, then rinsed with acetonitrile (ACN). These polished GC surfaces were used as cathodes for 10 min in the electrolysis of the solution containing

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

(23) Delamar, M.; Hitmi, R.; Pinson, J.; Saveant, J.-M. *J. Am. Chem. Soc.* **1992**, *114*, 5883.

(24) Andrieux, C.; Gonzalez, F.; Saveant, J.-M. *J. Am. Chem. Soc.* **1997**, *119*, 4292.

(21) Starkey, E. B. *Org. Synth.* **1939**, *19*, 40.

Table 1. Peak Potentials for Diazonium Reduction, Amine Precursors, and Deposition Potentials

| diazonium salt <sup>a</sup>       | amine precursor <sup>b</sup> | $E_p^c$ | $E_{mod}^d$ |
|-----------------------------------|------------------------------|---------|-------------|
| phenyl diazonium                  | aniline                      | -0.36   | -0.56       |
| 4-methyl phenyl diazonium         | 4-methyl aniline             | -0.36   | -0.57       |
| 4-trifluoromethylphenyl diazonium | 4-trifluoromethyl aniline    | -0.24   | -0.44       |
| 4-nitrophenyl diazonium           | 4-nitro aniline              | +0.04   | -0.16       |
| 4-ethyl phenyl diazonium          | 4-ethyl aniline              | -0.42   | -0.62       |
| 4-biphenyl diazonium              | 4-phenyl aniline             | -0.15   | -0.35       |
| 4-nitro azobenzene-4' diazonium   | 4-nitro, 4'-amino            | +0.01   | -0.19       |

<sup>a</sup> All are  $BF_4$  salts. <sup>b</sup> Amine from which diazonium salt was synthesized. <sup>c</sup> Voltammetric peak potential vs  $Ag/Ag^+$  for reduction of 1 mM diazonium salt in 0.1 M  $NBu_4BF_4$  in acetonitrile, 0.2 V/s. <sup>d</sup> Applied potential during formation of monolayer.

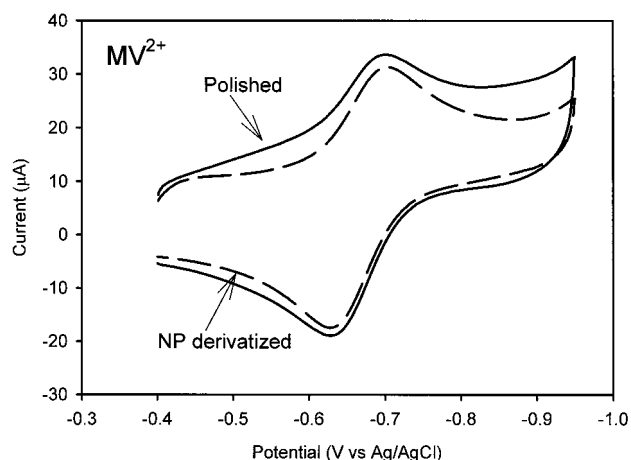


Figure 1. Cyclic voltammetry of 1 mM  $MV^{2+}$  in 0.1 M NaCl on polished GC (solid line) and GC following chemisorption of a nitrophenyl monolayer (dashed line). 0.2 V/s scan rate, no background subtraction.

1 mM of the appropriate diazonium salt and 0.1 M  $NBu_4BF_4$  in acetonitrile at a potential 200 mV negative of  $E_p$  for diazonium reduction. After derivatization, the GC electrodes were rinsed with electrolyte and sonicated in acetonitrile for 3 min and then in Nanopure water for 10 min. The peak potentials for diazonium reduction are listed in Table 1, along with the amine precursors, and deposition potentials.

## RESULTS

The simplest redox system studied in the current effort was the one-electron reduction of methyl viologen ( $MV^{2+}$ ) to its cation radical. This widely studied reaction is believed to be outer-sphere on carbon and diamond electrodes, forming a stable cation radical product.<sup>25</sup> A voltammogram for  $MV^{2+}$  on polished GC is shown in Figure 1, with the small  $\Delta E_p$  indicating fairly rapid electron transfer. Covalent modification of the GC with a nitrophenyl monolayer has little effect on the voltammetry, other than a slight decrease in background current. The  $k^0$  values for  $MV^{2+}/MV^+$ , determined from several repetitions of the experiment in Figure 1, are  $0.094 \pm 0.025$  cm/s ( $N = 3$ ) on polished GC and  $0.047 \pm 0.013$  cm/s ( $N = 3$ ) on the nitrophenyl modified GC surface. As

(25) Alehashem, S.; Chambers, S.; Strojek, J.; Swain, G.; Rajeshuni, R. *Anal. Chem.* **1995**, *67*, 2812.

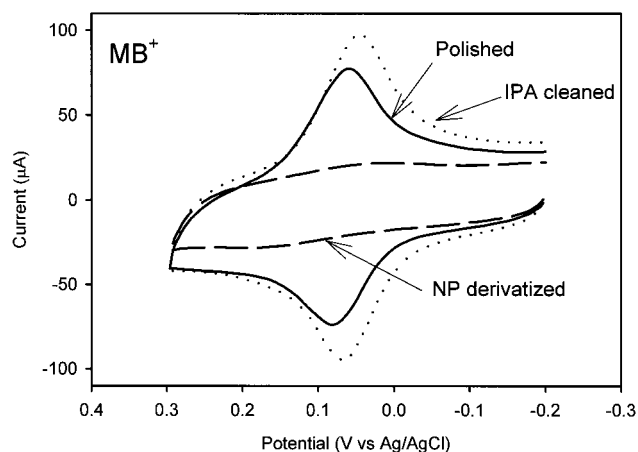


Figure 2. Voltammetry of 10  $\mu$ M methylene blue in 0.1 M  $H_2SO_4$ , 2 V/s, no background subtraction. Solid line is polished GC; dotted line is same electrode after cleaning with 2-propanol and activated carbon; dashed line is GC following nitrophenyl derivatization.

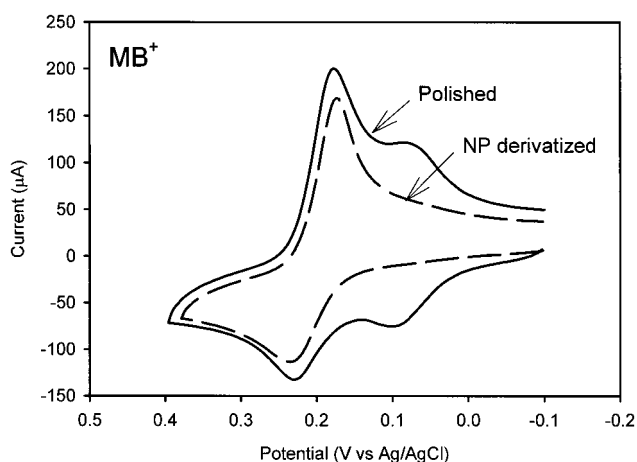


Figure 3. Voltammetry of 1 mM methylene blue in 0.1 M  $H_2SO_4$ , 2 V/s, no background subtraction. Solid line is polished GC, dashed is after nitrophenyl derivatization.

was the case with  $Ru(NH_3)_6^{+3/+2}$ , the nitrophenyl monolayer reduced  $k^0$  by a factor of 2, implying that both the  $MV^{2+}/MV^+$  and  $Ru(NH_3)_6^{+3/+2}$  systems are acting as outer-sphere redox reactions.

Methylene blue ( $MB^+$ ) is generally considered to undergo a reversible 2  $e^-$  reduction, but unlike  $MV^{2+}/MV^+$ ,  $MB^+$  is prone to adsorption on the GC surface.<sup>19</sup> Figure 2 shows voltammograms for  $MB^+$  at low concentration (10  $\mu$ M), at which the response is dominated by adsorbed  $MB^+$ . The voltammetric peak area corresponds to 213 pmol/cm<sup>2</sup> of  $MB^+$  adsorption, based on the geometric electrode area. Pretreatment of the polished GC surface with 2-propanol and activated carbon increases the coverage of  $MB^+$  on polished GC to 265 pmol/cm<sup>2</sup>, presumably due to surface cleaning.<sup>26</sup> However, a nitrophenyl monolayer completely suppresses observable  $MB^+$  adsorption. Increasing the  $MB^+$  solution concentration to 1 mM permits observation of diffusing as well as adsorbed  $MB^+$ . As shown in Figure 3, the diffusion wave centered at 0.2 V vs  $Ag/AgCl$  is distinguishable from the adsorption wave at  $\sim 0.08$  V. The nitrophenyl derivatization had little effect on the diffusion wave, but it suppressed adsorption. The voltammetry indicates that  $MB^+$  is also behaving as an outer-

(26) Ranganathan, S.; Kuo, T.-C.; McCreery, R. L., *Anal. Chem.*, in press.

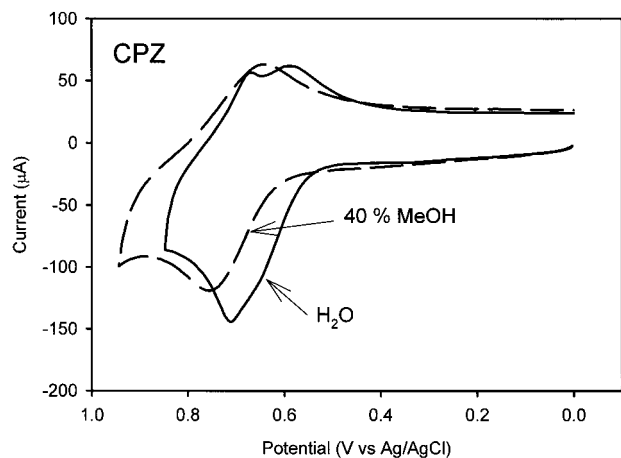


Figure 4. Voltammetry of 1 mM CPZ in 0.2 M NaCl containing 0.01 M HCl on polished GC in the absence (solid) and presence of 40% methanol. Two volts per second, no background subtraction.

sphere system, with a minor decrease in electron-transfer kinetics caused by a chemisorbed monolayer. Unlike  $MV^{+2}$ , however,  $MB^+$  exhibits adsorption which is strongly reduced by the presence of an otherwise inert monolayer. The asymmetry in the voltammetric peak heights for  $MB^+$  is presumably due to the more complex reaction mechanism, involving  $2 e^-$  and  $2 H^+$ .

Chlorpromazine (CPZ) and two related phenothiazines, promazine (PMZ) and trifluorpromazine (TPZ), are more complex redox systems than  $MB^+$  and  $MV^{+2}$  and were examined in much more detail. As described elsewhere, the initial oxidation product of CPZ, PMZ, or TPZ is a cation radical which reacts with water or buffer components to yield a sulfoxide.<sup>27–29</sup> To avoid these complicating reactions, the pH was adjusted to 2.0 with HCl. The cation radicals are stable in this medium on the time scale of a voltammogram, and the phenothiazines undergo a chemically reversible one-electron oxidation. A second complication for the phenothiazines is their tendency to adsorb on GC from aqueous solutions. This property was identified when CPZ electrochemistry was first examined in detail<sup>27</sup> and has been exploited for electroanalytical applications.<sup>30,31</sup> The adsorption appears to arise largely from the hydrophobic nature of the phenothiazine ring system and can largely be suppressed by adding 40% methanol to the electrolyte. Figure 4 shows voltammograms of CPZ at polished GC with and without 40% methanol. Methanol removes the obvious adsorption features but does not completely eliminate adsorption. Semi-integration of the CPZ voltammograms shows the slight peak on the semi-integral plateau which indicates adsorption,<sup>32</sup> even in the presence of 40% methanol. This adsorption is increased by pretreatment with 2-propanol and activated carbon, as was observed for  $MB^+$ . Furthermore, the adsorption of CPZ on polished GC adheres to a Langmuir isotherm determined with chronocoulometry (Figure 5). Saturation coverage of

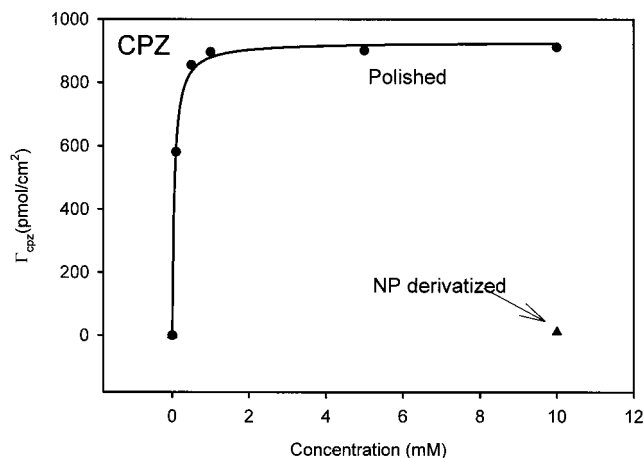


Figure 5. Adsorption isotherms for CPZ in 0.2 M NaCl, 0.01 M HCl, 40% MeOH. Abscissa is solution CPZ concentration,  $\Gamma_{CPZ}$  was determined from the Y intercept of chronocoulometric  $Q$  vs  $t^{1/2}$  plots, after subtraction of double-layer charge. Circles are polished GC surface, single triangle is from a nitrophenyl-modified surface. Line is a fit of polished data to a Langmuir isotherm ( $r^2 = 0.9980$ ).

93 pmol/cm<sup>2</sup> (based on geometric area) is reached at about 1 mM solution concentration. When the GC was derivatized with a nitrophenyl monolayer, the adsorption in 40% MeOH became negligible as measured by chronocoulometry even for 10 mM CPZ in solution (shown as triangle in Figure 5).

Unlike  $MB^+$ , CPZ adsorbed to the GC surface even when a nitrophenyl monolayer was present. With methanol absent, the slope of a  $\log(i_p)$  vs  $\log(\nu)$  plot (for 0.02 to 20 V/s) was 0.63 for CPZ on polished GC, well above the value of 0.50 expected in the absence of adsorption. A nitrophenyl monolayer reduced the slope to 0.56. However, the combination of 40% MeOH and the nitrophenyl monolayer decreased the slope to 0.509, implying greatly reduced adsorption. These results indicate that neither 40% MeOH nor nitrophenyl derivatization can completely suppress CPZ adsorption by themselves, but the combination can. The chronocoulometric results (Figure 5), the semi-integrals, and the slopes of  $\log(i_p)$  vs  $\log(\nu)$  plots all indicate that observable CPZ adsorption is suppressed for nitrophenyl derivatized surfaces in 40% MeOH.

The effects of various surface modifications on phenothiazine voltammetry were studied in the absence of methanol, initially, since these modifications had been characterized previously without methanol present.<sup>19</sup> CPZ, PMZ, and TPZ voltammograms were acquired at four scan rates (0.02, 0.2, 2, 20 V/s) on polished GC following several pretreatments. Anaerobic polishing with cyclohexane/alumina produced a GC surface with low surface oxide coverage.<sup>19</sup> AQDS (an anion), BMB, (neutral), and  $MB^+$  (a cation) were preadsorbed to polished GC before phenothiazine voltammetry. Previous results demonstrated that these adsorbates remain on GC after transfer to aqueous electrolyte from the adsorption solution.<sup>13,19</sup> The rate constants from these experiments are tabulated in Table 2, along with those for the nitrophenyl modified surface. In all cases,  $k^0$  did not show a significant trend with scan rate, and the standard deviations listed include the entire 0.02–20 V/sec range. Although some perturbation of these results is expected as a result of phenothiazine adsorption, Table 2 does demonstrate that the effects of surface derivatization are minor for all three phenothiazines. Surface-oxide coverage and the pres-

(27) Cheng, H. Y.; Sackett, P. H.; McCreery, R. L. *J. Am. Chem. Soc.* **1978**, *100*, 962.

(28) Cheng, H. Y.; Sackett, P. H.; McCreery, R. L. *J. Med. Chem.* **1978**, *21*, 948.

(29) Chapter 19. Mayausky, J. S.; Cheng, H. Y.; Sackett, P. H.; McCreery, R. L. ACS Advances in Chemistry Series 201; American Chemical Society: Washington, DC, 1982.

(30) Jarbawi, T. B.; Heineman, W. R. *Anal. Chim. Acta* **1982**, *135*, 57.

(31) Jarbawi, T. B.; Heineman, W. R.; Patriarche, G. *Anal. Chim. Acta* **1981**, *126*, 57.

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

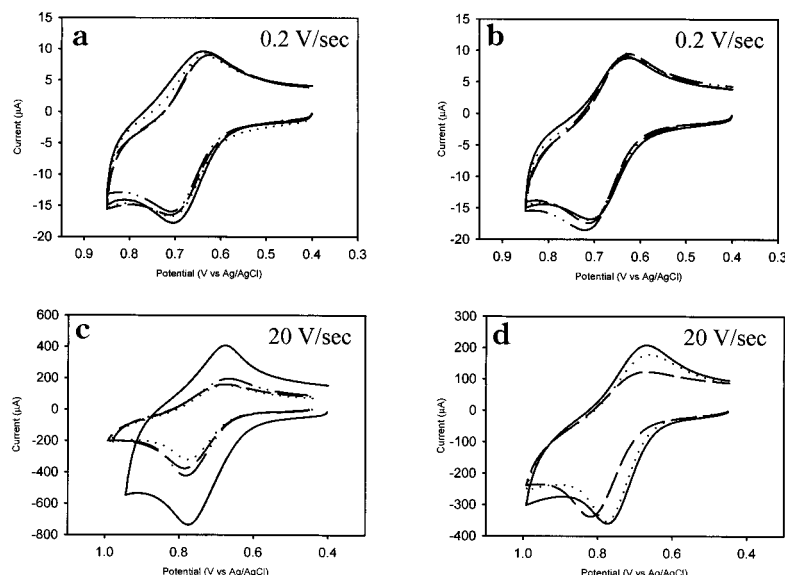


Figure 6. Voltammograms of CPZ on polished GC and six modified GC surfaces in 40% MeOH, containing 1 M NaCl, without background subtraction. Solid line in **a** and **c** is polished GC before derivatization, remaining curves in **a–d** are for the seven chemisorbed surfaces listed in Table 3. The dashed curve in **d** is the slowest surface observed (nitroazobenzene-modified GC).

Table 2.  $k^\circ$  of Chlorpromazine, Promazine, and Trifluorpromazine for Different GC Surfaces (0.2 M NaCl, 0.01 M HCl, No MeOH)

| $k^\circ$ (cm/s) <sup>a</sup> | chlorpromazine                     | promazine             | trifluorpromazine     |
|-------------------------------|------------------------------------|-----------------------|-----------------------|
| conventional polish           | 0.033 ± 0.003 <sup>b</sup><br>(44) | 0.026 ± 0.003<br>(12) | 0.023 ± 0.003<br>(20) |
| cyclohexane polish            | 0.034 ± 0.004<br>(24)              | 0.025 ± 0.003<br>(12) | 0.025 ± 0.003<br>(12) |
| AQDS preadsorbed              | 0.034 ± 0.002<br>(24)              | 0.026 ± 0.003<br>(12) | 0.023 ± 0.003<br>(12) |
| BMB preadsorbed               | 0.035 ± 0.002<br>(24)              | 0.027 ± 0.003<br>(12) | 0.025 ± 0.001<br>(12) |
| Methylene Blue preadsorbed    | 0.038 ± 0.002<br>(24)              | 0.027 ± 0.002<br>(12) | 0.023 ± 0.004<br>(12) |
| nitrophenyl derivatized       | 0.020 ± 0.003<br>(61)              | 0.014 ± 0.003<br>(12) | 0.013 ± 0.002<br>(12) |

<sup>a</sup> Obtained from the mean of  $k^\circ$  values determined at different scan rates (20 mV/s to 20 V/s). <sup>b</sup> Mean ± standard deviation. Parentheses indicate total number of measurements for four scan rates (0.02, 0.2, 2, and 20 V/s).

ence of anionic, neutral, or cationic adsorbers had little effect on the observed rates. Only a compact, chemisorbed monolayer of nitrophenyl groups has a significant kinetic effect, decreasing the rate constant by about 50%.

The covalently derivatized GC surfaces were examined in more detail, under conditions where adsorption was suppressed. Voltammetry for CPZ on a series of derivatized surfaces in 40% methanol is shown in Figure 7. Recall that in these conditions, the nitrophenyl surface showed no CPZ adsorption, and the CPZ electron-transfer rate constant was invariant with scan rate between 0.02 and 20 V/s. The polished, underivatized surface does show a larger  $i_p$  at 20 V/s, due to a contribution from adsorbed CPZ, but this effect is greatly reduced for low scan rate (0.2 V/s). The derivatization reagents were chosen to yield monolayers of increasing thickness, listed in Table 3. The distance between the GC surfaces and the monolayer/solution interface ( $d$ ) was calculated using molecular mechanics as described in Table 3, and represents the minimum distance between the surface and a

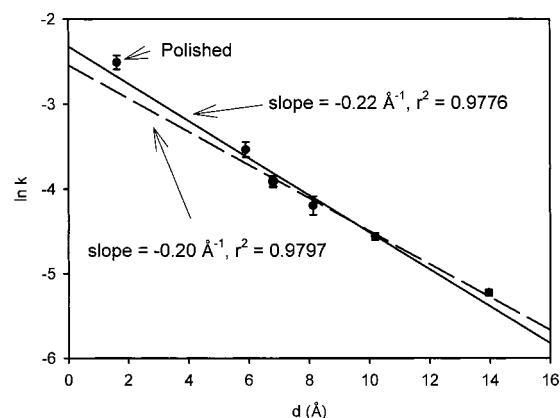


Figure 7. Plot of  $\ln(k^\circ)$  vs monolayer thickness ( $d$ , Å) listed in Table 3. Solid line includes underivatized surface ( $d = 1.6$  Å) in a linear least-squares fit, dashed line does not.

Table 3. CPZ Kinetic Results on Modified Surfaces

| monolayer             | $d$ , Å | $\Delta E_p$ for CPZ, mV, 0.2 V/s | $k^\circ_{CPZ}$            |
|-----------------------|---------|-----------------------------------|----------------------------|
| none                  | 1.6     | 63.3 ± 0.6                        | 0.081 ± 0.007              |
| phenyl                | 5.9     | 71.0 ± 1                          | 0.029 ± 0.003 <sup>b</sup> |
| methylphenyl          | 6.8     | 76.3 ± 1                          | 0.020 ± 0.001              |
| trifluoromethylphenyl | 6.8     | 77.0 ± 1                          | 0.020 ± 0.001              |
| nitrophenyl           | 6.8     | 76.7 ± 1                          | 0.020 ± 0.001              |
| ethylphenyl           | 8.1     | 81.3 ± 1.5                        | 0.015 ± 0.001              |
| biphenyl              | 10.2    | 88.7 ± 1.1                        | 0.010 ± 0.001              |
| nitroazobenzene       | 14.0    | 98.7 ± 1.1                        | 0.005 ± 0.001              |

<sup>a</sup> Tunneling distance calculated by Spartan software, structure optimized with molecular mechanics based on SYBYL force field. Van der Waals radius yielded  $d$  for polished GC of 1.6 Å. <sup>b</sup> Mean ± standard deviation for six determinations, all with a scan rate of 0.20 V/s.

redox system for a perfect monolayer. The observed rate constants and calculated  $d$  values are listed in Table 3. A plot of  $\ln(k^\circ_{CPZ})$  vs  $d$  is shown in Figure 8. The slope of the least-squares line for the derivatized surfaces is  $-0.20 \text{ Å}^{-1}$  ( $r^2 = 0.9797$ ) or  $-0.22 \text{ Å}^{-1}$  ( $r^2 = 0.9776$ ) if the point for the underivatized surface is included.

## DISCUSSION

Approximately 50 years of investigations into organic electrochemistry has established that electron transfer between solid electrodes and organic redox systems can involve complex interactions with the electrode surface. The many examples of adsorption and electrocatalysis accompanying organic redox reactions, combined with multiple electron and proton transfers present formidable hurdles to understanding organic redox kinetics and mechanisms. For carbon electrodes, one has the added complications of variable surface condition and a propensity to adsorb organic molecules from solution. Much of the motivation for the current effort is the objective of examining organic redox reactions on reproducibly prepared GC electrodes. Using the approach developed for inorganic redox systems,<sup>19</sup> surface modification of the GC can provide insight into surface variables affecting kinetics and adsorption. The redox systems chosen for this initial study are relatively simple, involving only one electron and no protons for MV<sup>2+/1+</sup>, CPZ, PMZ, and TPZ, with MB<sup>+</sup> following a more complex 2 e<sup>-</sup>/2 H<sup>+</sup> route.

Other than an apparently minor perturbation from MB<sup>+</sup> adsorption, MV<sup>2+/1+</sup> and MB<sup>+</sup> are remarkable in their insensitivity to surface modification. A nitrophenyl monolayer decreases the apparent  $k^{\circ}$ s by ~50% and completely blocks MB<sup>+</sup> adsorption. Clearly, MB<sup>+</sup> adsorption is not required for fast kinetics, and diffusing MB<sup>+</sup> undergoes fast electron transfer even when the GC surface is occupied by nitrophenyl groups. We concluded previously, for inorganic redox systems, that the electron tunnels through the nitrophenyl layer, causing a relatively small decrease in observed  $k^{\circ}$ .<sup>19</sup> Further evidence for the tunneling mechanism for the case of CPZ is discussed below.

Table 2 indicates the CPZ, PMZ, and TPZ electron-transfer kinetics are also insensitive to surface modification, even when adsorption is partly responsible for the observed current. The rate constants in Table 2 are suspect, due to adsorption, but the  $k^{\circ}$  values and the  $\Delta E_p$  results from which they were determined show no major changes with surface modifications. Adsorption and electron transfer are uncorrelated and apparently independent, a conclusion which is inconsistent with an electron-transfer mechanism involving electrocatalysis via a chemisorption or mediation mechanism. Like MB<sup>+</sup> and MV<sup>2+</sup>, the phenothiazines are behaving as outer-sphere systems with respect to electron transfer.

The uncertainties about the effects of adsorption on kinetic observations are greatly reduced for the covalently modified surfaces in the presence of 40% methanol. The adsorption of CPZ is presumably driven by dipole–dipole or  $\pi$ - $\pi$  interactions between the graphitic surface and the phenothiazine ring system, as well as hydrophobic effects. The nitrophenyl-modified surfaces show significantly weaker adsorption than a bare polished surface, apparently because direct interactions between the carbon surface and the phenothiazine ring are blocked. There is still some residual adsorption to the nitrophenyl/GC surface in the absence of methanol, presumably because hydrophobic effects are still present. The combination of nitrophenyl derivatization and 40% methanol reduces CPZ adsorption below levels detectable by chronocoulometry (Figure 5) or semi-integration.

The observed rate constants for CPZ obtained under conditions of negligible adsorption exhibit linear behavior in a plot of  $\ln k^{\circ}$  vs  $d$  (Figure 7). The point for polished GC at 1.6 Å is suspect due

to adsorption, but the error was minimized by using a low scan rate. For the polished surface, the addition of methanol increases the apparent  $k^{\circ}$  from 0.0333 (Table 2) to 0.081 (Table 3). The slope of the  $\ln k^{\circ}$  vs  $d$  plot of  $-0.22 \text{ Å}^{-1}$  (or  $-0.20$  if polished GC is not included) can be compared to the “tunneling parameter” ( $\beta$ ) discussed in studies of long-range electron transfer.<sup>33–37</sup> Equation 1 has been invoked to explain the dependence of the observed rate constant ( $k^{\circ}_{\text{app}}$ ) for metal electrodes modified with a self-assembled monolayer of thickness  $d$ :

$$k^{\circ}_{\text{app}} = k^{\circ} \exp(-\beta d) \quad (1)$$

$\beta$  depends on the tunneling mechanism and the chemical structure of the spacer, but values near  $1.0 \text{ Å}^{-1}$  have been proposed for through-bond tunneling in aliphatic chains and near  $1.3$ – $1.8 \text{ Å}^{-1}$  for through-space tunneling on modified gold electrodes.<sup>34</sup>  $\beta$  values for through-bond tunneling in unsaturated spacers in rigid molecules are substantially lower, ranging from  $0.14 \text{ Å}^{-1}$  for a conjugated polyene spacer to  $0.57 \text{ Å}^{-1}$  for phenyl-methylene spacers. The closest electrochemical analogy from the literature examined the distance dependence of electron transfer for phenylene/ethynyl spacers adsorbed to gold as thiolate monolayers.<sup>38</sup> For these conjugated spacers, the  $\beta$  value was  $0.57 \pm 0.02 \text{ Å}^{-1}$ . The adsorbates used to construct Figure 7 all have aromatic backbones and are conjugated when more than one ring is present. The observed  $\beta$  value of  $0.20 \text{ Å}^{-1}$  is within the range of  $0.14$ – $0.57 \text{ Å}^{-1}$ , expected for conjugated, unsaturated spacers. Under the assumption of through-bond tunneling, a  $\beta$  of  $0.20 \text{ Å}^{-1}$  is not unreasonable for the series of adsorbates considered here.

However, it is surprising that Figure 7 exhibits the linear  $\ln k^{\circ}$  vs  $d$  dependence expected for a tunneling mechanism in the first place. The chemisorbed monolayers are not expected to self-assemble on GC, since they are generated rapidly and their covalent bonds to the surface do not permit annealing. The initial GC surface is microscopically rough, so an ordered, regular monolayer is unlikely. However, the monolayers are likely to be low in pinholes, since any electroactive regions should have been covered by additional diazonium reduction during derivatization. The observed rate constants are reproducible to better than  $\pm 10\%$  for six determinations, in contrast to the large variation expected with a variable density of pinholes. Spectroscopic evidence indicates that diazonium reduction leads to compact monolayers with the aromatic ring axes perpendicular to the surface,<sup>14</sup> but it is conceivable that the monolayer films are thinner than predicted geometrically. Such a situation would yield an erroneously low value of  $\beta$ . The linearity of Figure 7 is consistent with a compact monolayer which tracks the shape of the rough GC surface and results in reasonably constant spacing between the GC substrate and the CPZ at the point of closest approach. However, the rather small  $\beta$  value of  $0.22 \text{ Å}^{-1}$  is considered

(33) Chidsey, C. E. D. *Science (Washington, D.C.)* **1991**, 251, 919.

(34) Finklea, H. O.; Hanshen, D. D. *J. Am. Chem. Soc.* **1992**, 114, 3173.

(35) Weber, K.; Creager, S. *Anal. Chem.* **1994**, 66, 3164.

(36) Tender, L.; Carter, M.; Murray, R. *Anal. Chem.* **1994**, 66, 3173.

(37) Bowler, B. E.; Raphael, A. L.; Gray, H. B. *Electron Transfer in Molecules and Proteins*. In *Progress in Inorganic Chemistry: Bioinorganic Chemistry*; Lippard, S. J., Ed.; Wiley: N. Y. 1990; Vol. 38, pp 259–322.

(38) Sachs, S. B.; Dudek, S. P.; Hsung, R. P.; Sita, L. R.; Smalley, J. F.; Newton, M. D.; Feldberg, S. W.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1997**, 119, 10563.

semiquantitative at present, given the uncertainties about surface-roughness effects and monolayer thickness.

There are several possible reasons why the phenothiazine electron-transfer reactions are fast compared with those of many organic redox systems, but a strong candidate for the major factor involves inner-sphere reorganization energy. It has long been recognized that redox reactions requiring significant changes in bond distances are often slow, due to the high reorganization energy accompanying electron transfer. For example,  $\text{Fe}(\text{H}_2\text{O})_6^{+3/+2}$  has a slow electron-exchange rate<sup>39</sup> and a small  $k^\circ$  on oxide-free carbon<sup>18</sup> because the Fe—O bond distance must change by 0.13 Å between  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ . Ferrocene (Fc) and anthracene are much faster, because delocalization of the positive charge upon oxidation leads to small changes in bond distances. For  $\text{Fc}/\text{Fc}^+$ , the bond lengths change by at most 0.04 Å upon oxidation.<sup>40–42</sup> The cation in  $\text{CPZ}^{*+}$  is quite delocalized, and one would not expect large bond-length changes during the  $\text{CPZ}/\text{CPZ}^{*+}$  redox reaction, or those of the related phenothiazines, PMZ, TPZ, and  $\text{MB}^+$ .

(39) Sutin, N. In *Inorganic Reactions and Mechanisms*; Zackerman, J. J., Ed.; VCH: Deerfield Beach, FL, 1986; Vol. 15; p 49ff.

(40) Seiler, P.; Dunitz, J. D. *Acta Crystallogr.* **1979**, B35, 1068.

(41) Lehmann, R. E.; Kochi, J. K. *J. Am. Chem. Soc.* **1991**, 113, 501.

(42) Webb, R. J.; Lowery, M. D.; Shiomi, Y.; Sorai, M.; Wittebort, R. J.; Hendrickson, D. N. *Inorg. Chem.* **1992**, 31, 5211.

(43) *Spartan*; software for ab initio geometry optimization; UHF-3TO-3G basis set.

Molecular-mechanics calculations<sup>43</sup> were used to estimate bond length changes for  $\text{Fc}/\text{Fc}^+$  and  $\text{CPZ}/\text{CPZ}^{*+}$ . The maximum change in bond length calculated for  $\text{Fc}/\text{Fc}^+$  was 0.05 Å, while that for  $\text{CPZ}/\text{CPZ}^{*+}$  was 0.04 Å. The small reorganization energy associated with small changes in bond length is likely to contribute to the fast kinetics observed for the phenothiazines, compared with those observed for many other organic redox systems.

In summary, the phenothiazines and  $\text{MV}^{2+/1+}$  behave as outer-sphere redox systems on GC and modified GC, with little kinetic sensitivity to surface modification. Chemisorbed monolayers greatly reduce phenothiazine adsorption, but have minor effects (~50%) on electron-transfer rates. The dependence of CPZ kinetics on monolayer thickness is consistent with a through-bond tunneling mechanism. More complex organic redox systems believed to involve chemisorption or proton transfer are currently under investigation on modified GC electrodes.

#### ACKNOWLEDGMENT

This work was supported by the National Science Foundation, Division of Analytical and Surface Chemistry.

Received for review March 2, 1999. Accepted June 28, 1999.

AC9902392