Effects of Redox System Structure on Electron-Transfer Kinetics at Ordered Graphite and Glassy Carbon Electrodes

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The basal plane of highly ordered pyrolytic graphite (HOPG) serves as an ordered model of more commonly used electrode surfaces such as glassy carbon (GC) and pyrolytic graphite. The defect density on the basal plane HOPG was reduced by careful cleaving and cell design and was verified to be low by requiring that ΔE_p for $Fe(CN)_6^{3-/4-}$ (1 M KCl) be greater than 700 mV for a 0.2 V/s scan rate. Then a variety of redox systems were examined on "validated" HOPG surfaces, and variations in the electron transfer rate constant, k_b^0, were observed. All 13 redox systems exhibited relatively fast kinetics on laser activated GC ($k^0 > 0.03$ cm/s for eight inorganic systems), and in several cases k^0 exceeded the instrumental limit. On HOPG, however, ΔE_p varied greatly for the 13 systems, ranging from 66 to >1200 mV. The reasons for this variation fall into three general classifications. First, reactions involving proton transfer (e.g. catechols) were all slow on HOPG, implying some role of the surface in mediating multistep processes. Second, the observed rate correlated with the exchange rate for homogeneous electron transfer, but the heterogeneous rates on HOPG were 3-5 orders of magnitude slower than that predicted from simple Marcus theory. Third, the physical properties of HOPG, such as density of electronic states and hydrophobicity, may depress k^0 relative to GC and metals.

INTRODUCTION

Due in part to the widespread use of carbon electrodes in electroanalysis and electrosynthesis, a large research effort has been invested in understanding heterogeneous electron transfer at carbon surfaces. Such investigations have dealt with effects of surface structure and pretreatment on electrochemical behavior for a variety of sp^2 carbon materials, including pyrolytic graphite, carbon paste, glassy carbon (GC), carbon films, and highly ordered pyrolytic graphite (HOPG).[1-5] The ultimate goal of electrode kinetic studies of such materials is elucidation of structure/reactivity relationships for carbon surfaces, with a specific goal of controlling electron-transfer rates. Achievement of these goals has been frustrated, however, by the complex nature of the carbon/solution interface caused by variability in surface history, particularly cleanliness, roughness, and the extent of oxide formation. Work in our lab and several others has demonstrated that reproducible kinetics are observable on GC with sufficient

attention to surface history.[6-12] In some cases, large changes in rate constants for benchmark redox systems can be effected reliably through laser activation,[8,10] heat treatments,[5,7] ultraclean polishing,[6] and electrochemical pretreatment.[13-16] However, since the structure of the carbon/solution interface after these procedures is ill-defined at the atomic level, it is currently difficult to deduce the structural factors which control electrode kinetics at the molecular level. Without a structurally well defined carbon surface, a rationale for how rates vary for different redox systems will be hard to formulate. Stated differently, structure/reactivity relationships derived from an incompletely characterized carbon surface will be ambiguous.

Ideally, one would like to survey a range of redox systems on an atomically well defined carbon surface. The basal plane of highly ordered pyrolytic graphite (HOPG) has potential for such correlations because of its well-defined structure and relative lack of surface impurities. HOPG was first used as an electrode by Yeager et al.,[17-19] and more recent work has demonstrated a large edge/basal plane rate anisotropy for several redox systems, with large voltammetric peak separations for $Fe(CN)_6^{3-/4-}$ and dopamine at the basal plane and near-reversible voltammetry at the edge plane.[1,20,21] HOPG has also been used as a substrate for the spectroscopy of adsorbates,[22] and its unusual adsorption properties and capacitance have been described.[23] It has not always been possible, however, to study heterogeneous electron-transfer kinetics at basal plane HOPG for a wide range of systems because of several experimental problems. Recently we have shown the dominating role of edge plane defects in various electrochemical processes. HOPG surfaces yield a wide range of results of $Fe(CN)_6^{3-/4-}$ kinetics, 2,6-anthraquinonedisulfonate (AQDS) adsorption, and differential capacitance,

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depending on surface defect density.[23,24] Capacitance ranging from 0.6 to 6.5 $\mu F/cm^2$, AQDS adsorption from <1.0 to 85 $pmol/cm^2$, and heterogeneous electron transfer rate constants for $Fe(CN)_6^{3-/4-}$ from 8×10^{-7} to 0.041 cm/s were obtained depending on the defect density of the surface.[23] It is clear, therefore, that without careful control of surface defects, highly variable rate constants can be obtained on the HOPG basal plane, impeding attempts to understand structure/reactivity relationships.

With an appreciation of the influence of defects on the electrochemical behavior of HOPG, it is possible to prepare low-defect basal surfaces which more accurately reflect the kinetics of the perfect, ordered surface. In the approach used here, we first validated a given HOPG basal surface by noting a very low k^0 for $Fe(CN)_6^{3-/4-}$. Since $Fe(CN)_6^{3-/4-}$ has a high ratio of edge to basal rates, a slow rate indicates minimal defect density. This *same* surface was then used to determine the rates for a variety of redox systems. Since the kinetic results were obtained on validated, low-defect surfaces, the surface-to-surface variability was greatly reduced and the rate comparisons were made on structurally better defined surfaces.

Heterogeneous electron transfer rates for 13 redox systems were determined at validated basal plane HOPG, high-defect density HOPG, and glassy carbon (GC). The results were used to assess the generality of the large edge/basal rate anisotropy and to infer structural variables affecting electrode kinetics at carbon electrodes.

EXPERIMENTAL SECTION

To minimize unintentional defects as well as air and solution exposure time, HOPG experiments were run in an inverted drop "cell" as reported earlier.[23] Ungraded HOPG (gift from Arthur Moore, Union Carbide) was cleaved either with ordinary "scotch" tape or with an Exacto knife blade edge. Best results were obtained when a thick (ca. 5-mm) piece of HOPG was cut perpendicular to the basal plane with a knife blade and the piece delaminated spontaneously. The cleaved piece was placed onto a conductive metal plate with graphite/Nujol paste serving to ensure good electrical contact. A drop of solution was placed onto the reference/auxiliary electrode couple which was then lowered onto a visually defect-free surface giving an effective electrode area of approximately 0.1 cm^2, as determined by $Fe(CN)_6^{3-/4-}$ chronoamperometry. The acronym HOPG is used henceforth to refer to the basal plane of low-defect HOPG unless noted otherwise.

In order to evaluate the relative defect density of freshly cleaved basal plane surfaces, voltammograms of 1 mM $K_4Fe(CN)_6$ or 1 mM $K_3Fe(CN)_6$ were obtained, in all cases in 1 M KCl with the inverted drop cell. Overall, the peak separation for $Fe(CN)_6^{3-/4-}$ at 0.2 V/s exhibited an average of 459 mV with a standard deviation of 331 mV and a range of 58–1200 mV. The large variability of ΔE_p for $Fe(CN)_6^{3-/4-}$ on HOPG indicates a large variation in adventitious defect density. In order to reduce this kinetic variability, a new surface was first validated with $Fe(CN)_6^{3-/4-}$ by requiring that ΔE_p be greater than 700 mV. After observing a ΔE_p >700 mV, the drop of $Fe(CN)_6^{3-/4-}$ solution was replaced with one of the redox system of interest, taking care to cover the same spot on the surface. It was noted that relatively thick (ca. 5-mm) pieces of HOPG yielded a higher "success rate" presumably due to greater mechanical rigidity. For the slower redox systems (ΔE_p >500 mV for basal plane) it was noted that the order of exposure to the test solution and $Fe(CN)_6^{3-/4-}$ affected ΔE_p, with ΔE_p increasing with air exposure or solution changes. The order of validation and test solutions was routinely reversed to check the effect on ΔE_p for the test systems. In all cases, the voltammetry for $Fe(CN)_6^{3-/4-}$ and the test redox system were completed within 1 min after the HOPG was cleaved.

The following redox systems (all in 1 M KCl unless noted otherwise) were used and are numbered here for reference in the figures: 1, 0.25 mM potassium hexachloroiridate(IV) (Aldrich Chemical Co.); 2, 1 mM hexammineruthenium(III) chloride (Strem Chemicals); 3, 2 mM tris(1,10-phenanthroline)cobalt(II) chloride (from 2 mM cobalt chloride hexahydrate (reagent grade, J. T. Baker Chemical Co.) and 6 mM 1,10-phenanthroline (reagent grade, J. T. Baker Chemical Co.)); 4, 1 mM methyl viologen ($MV^{2+/1+}$) (Sigma); 5, 2 mM tris(1,10-phenanthroline)iron(II) (from 2 mM ferrous ammonium sulfate (reagent grade, J. T. Baker) and 6 mM 1,10-phenanthroline); 6, 1 mM potassium ferrocyanide (J. T. Baker); 7, 10 mM tris(ethylenediamine)cobalt-(III) chloride (Johnson Matthey) + approximately 5 mM excess ethylenediamine (reagent grade, J. T. Baker); 8, 1 mM tris-(ethylenediamine)ruthenium(II) chloride (Johnson Matthey) in 0.2 M $HClO_4$. $HClO_4$ was used in the case of $Ru(en)_3^{2+/3+}$ to avoid degradation by air.[25]

Quinone systems included: 9, 1 mM AQDS (Aldrich) in 0.1 M H_2SO_4; 10, 1 mM dopamine (Aldrich) in 0.1 M H_2SO_4; 11, 1 mM 4-methylcatechol (Aldrich) in 0.1 M H_2SO_4; 12, 1 mM dihydroxy-phenylacetic acid (DOPAC, Aldrich) in 0.2 M $HClO_4$, 13, 6-hydroxydopamine (Sigma) in pH 7 phosphate buffer and 1 M KCl. All solutions were prepared daily with distilled Nanopure water (Barnstead) and degassed with argon.

For inverted drop experiments, either a silver wire quasi-reference electrode (QRE) or a Ag/AgCl (3 M NaCl) electrode with a capillary salt bridge was used. The potential of the QRE was typically 0 to –5 mV vs SSCE, but in all cases only ΔE_p was determined when the QRE was used, so an absolute potential was not required. Reference electrodes for GC experiments were either Ag/AgCl or sodium-saturated calomel (SSCE), but all $E_{1/2}$ values are reported relative to the SSCE. Laser irradiation (50 MW/cm^2) of HOPG was conducted either in situ as described previously[20,21] or ex situ with immediate replacement of solution. Ex situ experiments were run by directing the laser beam through two right-angle prisms onto an inverted drop "cell". Solution was removed prior to and replaced immediately following irradiation. Glassy carbon electrodes (with areas of (2–5) × 10^{-3} cm^2) were prepared as described previously[8] from a GC-20 plate (Tokai) and embedded in epoxy (Eccobond 55, Emerson and Cuming, Inc.) The GC electrodes were polished conventionally and laser-irradiated (25 MW/cm^2) in solution as described previously.[8]

For scan rates of 0.2–20 V/s, linear sweep voltammetry was performed with a computer-triggered function generator (Tektronix) and "Labmaster" A/D converter. For faster scans, data were collected with a digital oscilloscope (Lecroy 9400A), with triggering and data transfer accomplished via locally written software. A conventional three-electrode potentiostat (Advanced Idea Mechanics, Columbus, OH) was used for all voltammetry, with the RC filter value maintained such that $RCn\nu < 4$ mV.[26]

GC voltammetry was performed with scan rates of 0.2–100 V/s, and rate constants were calculated using the method of Nicholson.[27] In several cases, the GC rate constants were sufficiently large that the ΔE_p approached the reversible limit of 57/n mV. For these cases, the rate constant evaluated from ΔE_p was a lower limit. In no case was ΔE_p for laser-activated GC greater than 150 mV. For validated HOPG, large ΔE_p values bring into question the assumptions of constant transfer coefficient (α) underlying Nicholson's approach, so rate constants were calculated both from ΔE_p and by the approach of Corrigan and Evans.[28] Experimental voltammograms were compared with those simulated with potential-dependent α. Unless noted otherwise, all HOPG rate constants were determined from the best fit to simulated voltammograms with potential-dependent α. For GC, ΔE_p was sufficiently small that a potential-dependent α was unnecessary for an accurate simulation and rate constants determined from simulations equaled those calculated with the Nicholson approach. The experimentally determined rate con-
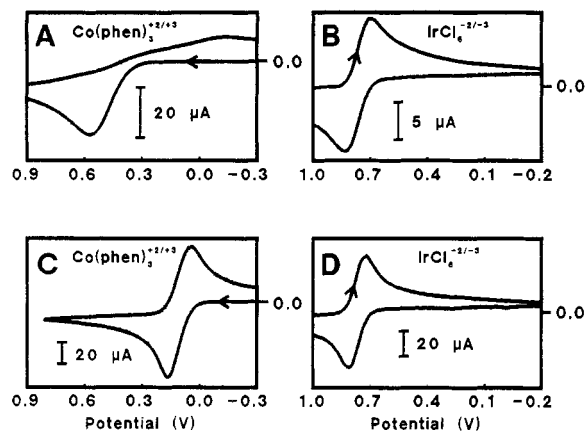
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Figure 1. Voltammetry at validated basal plane HOPG for (A) 2 mM Co(phen)$_3^{2+/3+}$, 1 M KCl; (B) 0.25 mM IrCl$_6^{2-/3-}$, 1 M KCl; and at high-defect density HOPG for (C) Co(phen)$_3^{2+/3+}$; (D) IrCl$_6^{2-/3-}$. Scan rate = 0.2 V/s. Potentials are vs Ag QRE.

stants for laser-activated GC are denoted k_{GC}^0, the experimental rate constants for validated basal plane HOPG determined from comparison to simulation are k_b^0, and those for laser activated HOPG are k_{las}^0. The small background currents for HOPG voltammograms were not subtracted before plotting or analysis.

Diffusion coefficients for solutions listed above were determined by chronoamperometry with a GC electrode of known area. A 5-s time scale was used, and background subtraction was utilized. For methyl viologen and Ru(en)$_3^{3+/2+}$, chronoamperometric response was slightly nonideal, apparently due to adsorption, and D_{ox} was assumed to equal 5×10^{-6} cm^2/s. $E_{1/2}$'s for each system were determined as the average of the oxidation and reduction peak potentials for GC voltammograms with scan rates at which the systems were nearly reversible.

RESULTS

Figure 1 shows the importance of defects to the observed voltammetry and illustrates a marked difference in the behavior of two inorganic redox systems. Voltammograms A and B were obtained on HOPG surfaces which met the validation criterion. Voltammogram A is for Co(phen)$_3^{2+/3+}$ on a surface for which ΔE_p of Fe(CN)$_6^{3-/4-}$ was 900 mV, and B is for IrCl$_6^{2-/3-}$ on a surface exhibiting a ΔE_p for Fe(CN)$_6^{3-/4-}$ of 1200 mV. Note the large difference in ΔE_p for the two systems, indicating a much smaller k_b^0 for Co(phen)$_3^{2+/3+}$ than for IrCl$_6^{2-/3-}$. Voltammograms C and D were obtained on surfaces which failed the validation criterion, exhibiting ΔE_p values for Fe(CN)$_6^{3-/4-}$ of 455 and 58 mV, respectively. Note that a decrease in ΔE_p for Fe(CN)$_6^{3-/4-}$ for the surfaces of Figure 1A and 1C from 900 to 445 mV had a large effect on ΔE_p for Co(phen)$_3^{2+/3+}$, implying that Co(phen)$_3^{2+/3+}$ is very sensitive to defects and has a high edge/basal rate ratio. However, an even larger change for the surfaces of Figure 1B and 1D (1200 to 58 mV) had only a slight effect on ΔE_p for IrCl$_6^{2-/3-}$. IrCl$_6^{2-/3-}$ is only slightly faster on a quite defective surface, implying that the basal plane rate is not greatly slower than the edge plane rate. The variation in ΔE_p for Fe(CN)$_6^{3-/4-}$ and various redox systems is shown in Table I for validated surfaces. Significant surface-to-surface variation was observed for Fe(CN)$_6^{3-/4-}$, presumably due to variations in the small residual defect density. This variation confirms the high sensitivity of Fe(CN)$_6^{3-/4-}$ kinetics to defect density. For the systems listed in Table I, the range in ΔE_p among different systems is much greater than the variation for a given system.

Several voltammograms of different redox systems on validated HOPG are exhibited in Figure 2. Note the variety of peak separations and voltammogram shapes. Unusual voltammogram shapes are particularly evident for systems

with low k_b^0. We have reported earlier that for Fe(CN)$_6^{3-/4-}$, the voltammogram shape at low-defect HOPG could be fit to simulations that involve a potential-dependent transfer coefficient.[23] We note here that simulations with potential-dependent α do fit the experimental data better for certain systems, but there is still a degree of divergence from theory. For systems with peak separations < 150 mV, simulations with constant α fit well to experimental data. In Figure 3A, experimental data for Co(en)$_3^{2+/3+}$ are compared to a simulation in which α is varied with potential. Note that this best fit to the anodic wave still does not completely match the experimental curve. In Figure 3B, however, Fe(phen)$_3^{2+/3+}$ voltammetry agrees well with the simulation, with a constant α. Results for all systems examined are summarized in Table II. As an additional measure of edge/basal rate anisotropy for HOPG, rate constants for laser-activated HOPG are included in Table II. In all cases, k^0 was larger on laser-damaged HOPG, often by several orders of magnitude.

In order to provide a reference carbon surface for comparison, rate constants for the eight inorganic systems and MV$^{1+/2+}$ were determined on the more commonly studied GC. Polished GC surfaces have been shown to yield very irreproducible rate constants, apparently due to surface impurities.[1,5,6,8] Laser activation of polished GC yields reproducible rate constants for Fe(CN)$_6^{3-/4-}$, comparable to those observed at heat-treated and fractured GC.[1,8,29] Thus laser-activated GC provides a carbon surface with reproducible kinetics with which to compare the behavior on HOPG for the redox systems examined. GC is also a more practical reference surface than edge plane HOPG due to the difficulty of reproducing the fragile edge plane surface.[21] In some cases, adsorption or ohmic potential error prevented the use of sufficiently high scan rates to determine k_{GC}^0 accurately. However, in all cases the ΔE_p observed on GC was lower than that on validated HOPG. As shown in Table II, the difference in rate constants between HOPG and GC was large in some cases, confirming and extending the rate anisotropy observed for Fe(CN)$_6^{3-/4-}$.

DISCUSSION

Considering the results in general terms initially, the most striking observation is the wide range of observed peak separations on validated HOPG, listed in Table II. In many cases, redox systems which exhibit fast electron transfer on GC or damaged HOPG, e.g. dopamine, Fe(CN)$_6^{3-/4-}$, and Co(phen)$_3^{2+/3+}$, are very slow on low-defect HOPG. For all 13 systems examined, the GC rates were faster than validated HOPG rates. On the basis of previous spectroscopic and microstructural information, we have concluded that this difference is due to the greater reactivity of graphitic edge regions compared to ordered basal plane,[1,8,20,21] although this conclusion was initially based on a limited number of redox systems. Since GC surfaces are rich in edge sites, their electrochemical kinetic behavior is similar to edge plane HOPG rather than basal plane.

Given the observation of a large edge/basal or GC/basal rate difference for at least the 13 systems studied, several questions arise. First, are the observations perturbed by some technical problems such as instrumentation limits, residual defects on the validated surface, etc.? Second, are there mechanistic differences among the 13 systems which cause the wide variations in rate? Third, for redox systems with apparently similar charge transfer mechanisms, what controls the rate on HOPG?

One technical limitation is easily recognized from the large k^0 values observed on GC. Fabrication of the GC electrodes

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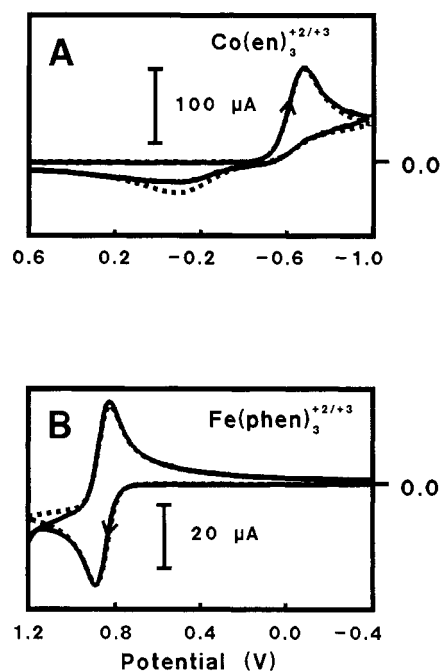
Table I. Peak Separations on Validated HOPG Surfaces

system	ΔE_p (mV) system[a]	ΔE_p (mV) $Fe(CN)_6^{3-/4-}$	k_N^0 [b] (cm/s) (system)	k_b^{0} [c] (cm/s) (system)	α (dα/dE)
1 $IrCl_6^{2-/3-}$	137	1200	0.0034	0.0034	0.50
	145	910	0.0029		(0.0)
	$\overline{96}$	1160	$\underline{0.0083}$		
	$\overline{126} \pm 27$		$\overline{0.0049} \pm 0.003$		
2 $Ru(NH_3)_6^{2+/3+}$	285	1230	5.6×10^{-4}	9×10^{-4}	0.50
	215	1370	1.0×10^{-3}		(0.0)
	158	1185	2.2×10^{-3}		
	$\underline{167}$	1175	$\underline{2.0 \times 10^{-3}}$		
	$\overline{206} \pm 58$		$\overline{1.4 \times 10^{-3}} \pm 8 \times 10^{-4}$		
3 $Co(phen)_3^{2+/3+}$	715	900	8.0×10^{-6}	2×10^{-5}	0.50
	675	725	1.3×10^{-5}		(0.25 V^{-1})
	600	940	2.6×10^{-5}		
	$\underline{695}$		$\underline{9.5 \times 10^{-6}}$		
	$\overline{671} \pm 50$		$\overline{1.4 \times 10^{-5}} \pm 8 \times 10^{-6}$		
4 $MV^{1+/2+}$	76	1235	0.017	0.017	(0.50)
	63	981	>0.075		(0.0)
	$\underline{65}$	1080	$\underline{>0.054}$		
	$\overline{68} \pm 7$		$\overline{>0.049} \pm 0.029$		
5 $Fe(phen)_3^{2+/3+}$	63	1300	>0.075	>0.075	0.50
	57	1045			(0.0)
	60	1024			
	$\underline{66}$	945	$\underline{>0.042}$		
	$\overline{62} \pm 4$		$\overline{>0.059}$		
7 $Co(en)_3^{2+/3+}$	770	695	5.4×10^{-6}	2×10^{-5}	0.65
	711	1230	9.3×10^{-6}		(0.17 V^{-1})
	$\underline{790}$	938	$\underline{4.2 \times 10^{-6}}$		
	$\overline{757} \pm 41$		$\overline{6.3 \times 10^{-6}} \pm 2.7 \times 10^{-6}$		
8 $Ru(en)_3^{2+/3+}$	502	1085	7.0×10^{-5}	1.3×10^{-4}	0.62
	373	883	2.3×10^{-4}		(0.0)
	$\underline{307}$	1135	$\underline{4.5 \times 10^{-4}}$		
	$\overline{394} \pm 99$		$\overline{2.5 \times 10^{-4}} \pm 1.9 \times 10^{-4}$		

[a] All data at 200 mV/s. [b] Determined from ΔE_p by method of Nicholson.[27] [c] Rate constant calculated by comparison to simulations, with α and dα/dE shown.
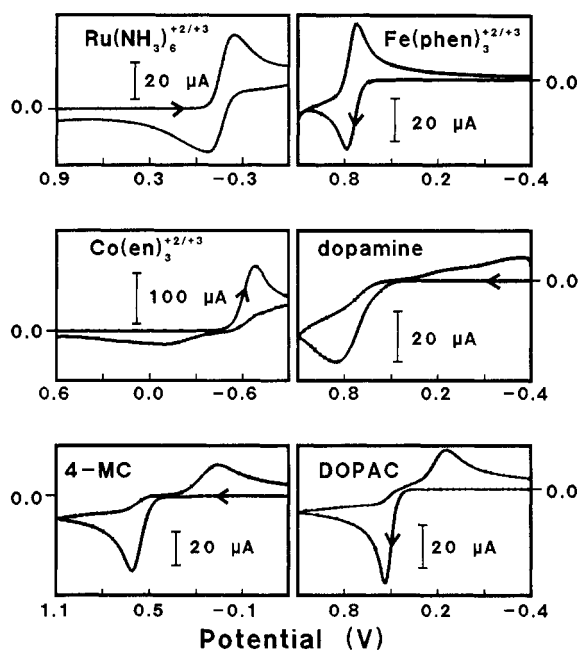
Figure 2. Voltammetry at validated basal plane HOPG: 1 mM $Ru(NH_3)_6^{2+/3+}$, 1 M KCl; 2 mM $Fe(phen)_3^{2+/3+}$, 1 M KCl; 10 mM $Co(en)_3^{2+/3+}$, 1 M KCl; 1 mM dopamine, 0.1 M H_2SO_4; 1 mM 4-methylcatechol (4-MC), 0.1 M H_2SO_4; 1 mM DOPAC, 0.2 M $HClO_4$. Scan rate = 0.2 V/s. Potentials are vs Ag QRE.

Figure 3. Voltammetry at validated basal plane HOPG. Solid lines are experimental data in both cases. (A) 10 mM $Co(en)_3^{2+/3+}$, 1 M KCl. Dashed line simulated for $k^0 = 2 \times 10^{-5}$ cm/s, $\alpha_0 = 0.65$, dα/dE = 0.17 V^{-1}. (B) 2 mM $Fe(phen)_3^{2+/3+}$, 1 M KCl. Dashed line simulated for $k^0 = 0.11$ cm/s, $\alpha_0 = 0.5$, dα/dE = 0.0 V^{-1}. Scan rate = 0.2 V/s. Potentials are vs Ag QRE.

from well-characterized GC stock results in electrode surfaces with minimum dimensions of about 0.5 mm × 0.5 mm. Ohmic potential error limits the useful scan rate to about 500 V/s, resulting in an upper limit of observable k^0 on GC of about

0.5 cm/s.[8] In a previous publication, these electrodes were shown to yield reliable k^0 values of 0.5–0.8 cm/s at 100–500 V/s, but larger k^0 values are difficult to measure without

Table II. Composite Redox Potential and Kinetic Data

	system	$E_{1/2}^a$ (V vs SSCE)	ΔE_p^b (mV)	k_b^0 (cm/s)	$k_{las}^{0\ c}$ (cm/s)	$k_{GC}^{0\ d}$ (cm/s)	$k_{GC}^0/k_b^{0\ e}$	k_{exc}^f (M^{-1} s^{-1})	ref
1	IrCl$_6^{2-/3-}$	0.74	146	0.003	0.05	>0.5	>200	2×10^5	47
2	Ru(NH$_3$)$_6^{2+/3+}$	−0.19	285	9×10^{-4}	0.05	>0.4	>400	4000	25, 48
3	Co(phen)$_3^{2+/3+}$	0.10	715	2×10^{-5}	0.002	0.08	4000	40	49
4	MV$^{1+/2+}$	−0.67	76	0.017		>0.1	>6	10^7	50
5	Fe(phen)$_3^{2+/3+}$	0.86	66	>0.07		>0.2	>6	3×10^8	51
6	Fe(CN)$_6^{3-/4-}$	0.25	700–1370	$10^{-6\ g}$	0.05	>0.6	$>6 \times 10^5$	2×10^4	52, 53
7	Co(en)$_3^{2+/3+}$	−0.48	770	2×10^{-5}	0.001	0.03	2000	8×10^{-5}	54
8	Ru(en)$_3^{2+/3+}$	−0.08	502	1×10^{-4}		>0.5	>5000	4000	48
9	AQDS	−0.14	870						
10	dopamine	0.51	1200						
11	4-methylcatechol	0.40	460						
12	DOPAC	0.31	370						
13	6-hydroxydopamine	−0.31	840						

^{a} Average of voltammetric peak potentials on laser activated GC. ^{b} On validated HOPG basal plane surfaces. ^{c} Laser-activated HOPG, after three 50 MW/cm^2 pulses ex situ. ^{d} Laser-activated GC, after three 25 MW/cm^2 pulses in situ. ^{e} Ratio of laser-activated GC rate constant to validated HOPG rate constant. ^{f} Homogeneous self-exchange rate, with literature reference. ^{g} Value for HOPG surface exhibiting minimum AQDS adsorption, from ref 23.

smaller electrodes.[8] Therefore, GC rate constants reported as 0.2–0.6 cm/s here should be considered lower limits and could in fact be significantly higher. For HOPG examined with the inverted drop, the electrode area is larger, but k^0 is much smaller and high scan rates were not required. Thus the HOPG rate constants are not subject to significant error from solution iR effects. In addition, the relatively high c-axis resistivity of HOPG (0.17 Ω-cm) would yield a typical resistance in the ca. 3-mm-thick pieces of HOPG used here of about 0.3 Ω, not enough to contribute significant ohmic potential error.

A second potential technical problem arises from uncertainty about residual defects on the validated HOPG surface. As noted earlier, the large standard deviation for ΔE_p of Fe(CN)$_6^{3-/4-}$ on unvalidated surfaces indicates that adventitious defects can drastically affect observed kinetics. The requirement that ΔE_p for Fe(CN)$_6^{3-/4-}$ exceed 700 mV significantly reduces this variability (Table I), but it is still possible that residual defects contribute to the apparent k_b^0 on HOPG. Since the rates on GC or edge plane graphite are all faster than those on validated HOPG, residual defects will increase the apparent k_b^0. Strictly speaking, the k_b^0 values measured on validated surfaces are upper limits for the true basal plane k^0 values. However, more can be concluded from the data in Table I. The observed ΔE_p values for the test systems vary much less (and often in different directions) than the Fe(CN)$_6^{3-/4-}$ values, implying no correlation of ΔE_p with defect density on validated surfaces. Furthermore, ΔE_p varies greatly for test systems (e.g. 62 mV for Fe(phen)$_3^{2+/3+}$ vs 670 mV for Co(phen)$_3^{2+/3+}$) on surfaces with similar Fe(CN)$_6^{3-/4-}$ voltammetry. These observations demonstrate that the large differences in observed kinetics among the systems examined on validated surfaces cannot be a consequence solely of residual defects.

A related issue is possible distortions to voltammetry caused by nonplanar diffusion to defects, possibly leading to microelectrode array behavior. As discussed previously,[23] the assumption of planar diffusion will break down if the spacing between defects is comparable to or greater than $(Dt)^{1/2}$, where D is the diffusion coefficient and t is electrolysis time. Such distortions are unlikely to occur for validated HOPG surfaces, however, both because the scan rates used for HOPG are relatively slow (yielding a relatively large $(Dt)^{1/2}$) and because the validation procedure reduces the density of defects to very low levels.

Speaking more quantitatively, the fact that the k_b^0 values are upper limits and the k_{GC}^0 are lower limits indicates that the rate anisotropy between edge and basal plane is at least as large as that reported in Table II. For the purposes of this

study, it is sufficient to conclude that all redox systems studied are slower on basal plane HOPG than on GC and that the anisotropy varies greatly from system to system. The precise magnitude of the anisotropy will remain uncertain as long as residual defects are possible.

A final technical issue to be considered here deals with the effect of impurity adsorption on observed kinetics, which is at least one of the important variables for GC.[5–8,29] Although basal HOPG surfaces were examined within 1 min of cleaving, some exposure to air and solution impurities was unavoidable. It was observed that k_b^0 for "fast" systems (ΔE_p < 400 mV) did not vary greatly with time of air or solution exposure, while those with slow kinetics (ΔE_p > 400 mV) exhibited an increasing ΔE_p with time. This observation is consistent with adsorption of impurities to *defects* rather than to basal plane, as is observed with intentional adsorbers such as AQDS.[23] Taken together, these technical concerns reinforce the conclusion that k_{GC}^0 values are lower limits of the true GC rate constants, while k_b^0 values are upper limits for the true basal plane HOPG rate constants. In addition, any errors in k_b^0 caused by residual defects or impurities will be most important for the slowest redox systems.

Let us now turn to the question of the origin of the often large differences between HOPG and GC rates. It is useful to note initially that most of the 13 systems studied exhibit fast electron transfer on laser-activated GC. Past experience with GC in several laboratories indicates that observed kinetics are very sensitive to surface history, with k_{obs}^0 varying by several orders of magnitude for dopamine or Fe(CN)$_6^{3-/4-}$ for nominally similar GC electrodes with varying pretreatment.[1,4–16] For the laser-activated GC surface, however, the rates are consistently fast, often at the instrumental limit for rate constant determination. There may be significant variations in k_{GC}^0 which are masked by the instrumental limit, but clearly the rates are high with only a few exceptions.

In contrast, basal rates for all systems are slower and cover a wider range. The inorganic complexes exhibit a k_b^0 on validated surfaces ranging from <10^{-6} to >0.07 cm/s, while the organic systems have ΔE_p's from 76 to 1200 mV. A possible origin for these variations is differences in mechanism which may involve specific surface chemical interactions. For example, if electron transfer requires a functional group which is present only on edge plane defects, it should be very slow on basal plane. Considering Table II, it is clear that all of the organic systems with multistep electron transfer mechanisms involving protons are slow (ΔE_p > 450 mV) on basal plane. There could be several mechanisms which promote fast electron transfer at defects for reactions involving protons. Cabaniss et al. proposed a proton-assisted electron-transfer
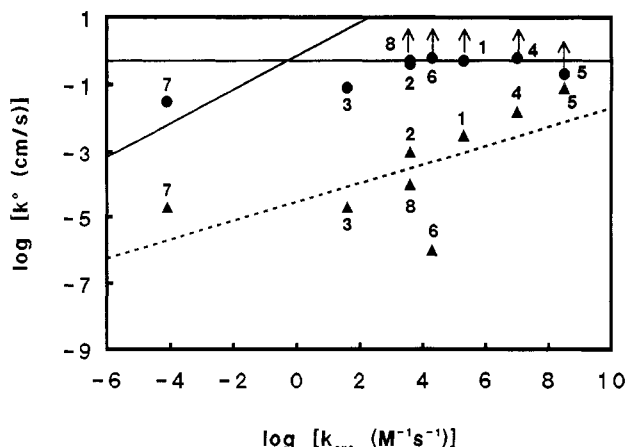
Figure 4. Log–log plot for rate constants versus homogeneous self-exchange rates (k_{exc}) for one-electron systems. Triangles are validated HOPG heterogeneous rate constants. Circles are laser-activated GC rate constants. Solid line is from Marcus theory, eq 1 in text. Dashed line is least squares fit for all points, HOPG data: slope = 0.29, y-intercept = –4.5, correlation coefficient = 0.66 Horizontal line indicates upper limit of measurable rate constants for GC experiments, k^0 = 0.5 cm/s. Data and number assignments from Table II.

route, which would be prevented on perfect basal plane.[14] It could be that proton transfer occurs between a protonated edge plane surface group (or merely adsorbed protons) and the redox system, thus accelerating electron transfer at defects or on GC. There are several other possible mechanisms, but it is clear that all five reactions studied here which involve protons are very slow on basal plane HOPG and fast on defects or GC.

After eliminating the systems with obvious proton involvement, there remain seven inorganic complexes and $MV^{2+/1+}$. These systems all involve one-electron transfers with no major changes in coordination geometry. The reasons for large rate differences between GC and HOPG for these systems should fall into two classes. First, the redox systems may vary in mechanism or homogeneous self-exchange rate (k_{exc}), thus affecting their kinetics with presumably any electrode material. Second, the reason may involve the nature of HOPG itself, particularly some difference in physical properties between basal plane HOPG and GC. Considering the redox systems first, we may suspect $Fe(CN)_6^{3-/4-}$ to be unusual because of the well-known involvement of K^+ in electron transfer.[30,31] It has been concluded that K^+ is involved in the $Fe(CN)_6^{3-/4-}$ transition state and that variations in cation identity and concentration strongly affect the observed rate. It is possible that this K^+ effect requires edge plane sites and cannot operate on basal plane, thus leading to very low basal rates. The large decrease in k_{GC}^0 for $Fe(CN)_6^{3-/4-}$ by intentional anthraquinone adsorption[32] reinforces the importance of surface sites for fast kinetics of $Fe(CN)_6^{3-/4-}$ at carbon.

The relationship between k_{GC}^0, k_b^0, and homogeneous self-exchange rate, k_{exc}, is plotted in Figure 4. Marcus proposed the simplest form of the relationship between k^0 and k_{exc} (eq 1), which is expected to apply in the absence of work terms

introduced by the electrode:[33-36]

$$(k_{exc}/Z_{exc})^{1/2} = k^0/Z_{el} \qquad (1)$$

where Z_{exc} and Z_{el} are the associated frequency factors (usually taken as 10^{11} M^{-1} s^{-1} and 10^4 cm s^{-1}, respectively). Several investigations support eq 1 for Hg and Pt electrodes for a variety of apparently outer sphere redox systems.[35-38] As pointed out by Weaver, however, eq 1 neglects several potentially important work terms which lead to generally smaller k^0 values than those predicted from eq 1.[39-41] Weaver's treatment predicts a linear dependence of work-corrected log k_{obs}^0 on log k_{exc}, with a slope of 0.5. Since the k_{GC}^0 values are at or near the instrumental limit, no correlation could be observed with k_{exc} for GC electrodes. Ignoring $Fe(CN)_6^{3-/4-}$, the seven apparently uncomplicated systems show a trend with k_{exc} (Figure 4), but the k_b^0 values are 3–5 orders of magnitude lower than that predicted from eq 1. In the absence of some unknown mechanistic complication which requires edge sites, this rate shortfall must be caused either by much larger work terms for HOPG or by some physical property of HOPG, or both.

Basal plane HOPG differs from GC in several ways which could affect electron-transfer kinetics. It is hydrophobic,[42,43] has a relatively high resistance normal to the surface,[1] has a low density of electronic states compared to metals or GC,[44,45] and has unusual double layer effects related to its semimetal character.[17-19,44,45] While the list of "uncomplicated" systems is too short to establish the relative importance of these effects on basal plane kinetics, some observations deserve note. First, hydrophobic effects cannot be the sole cause of slow kinetics since systems of similar charge and structure, and presumably hydrophobicity (e.g., $Fe(phen)_3^{2+/3+}$ and $Co(phen)_3^{2+/3+}$), have very different rates. Furthermore, basal rates are largely independent of redox system charge. Second, the c-axis resistivity of HOPG would yield less than 1 Ω of uncompensated resistance and would be roughly equal for all systems. Third, any unusual double layer or space charge effects for basal plane should vary greatly with the potential relative to the pzc.[17-19,44,45] The pzc for HOPG has been reported as –0.24 V vs SSCE for a variety of aqueous electrolytes,[17-19] and that value was confirmed here for 1 M KCl. As shown in Figure 5, the observed rates show no obvious perturbations when $E_{1/2}$ is near the pzc, with fast and slow rates observed on either side of the pzc. So space charge capacitance (and associated potential drop) and double layer effects are unlikely to be the sole reasons for low k_b^0. Fourth, the low density of states (DOS) near the Fermi level of HOPG could slow down electron transfer relative to GC. According to Gerischer et al.[45] the DOS for HOPG reaches a minimum of 2.2 × 10^{-3} states atom^{-1} eV^{-1} at the bulk Fermi level of graphite but increases rapidly away from this potential. This minimum is approximately 2 orders of magnitude lower than that of

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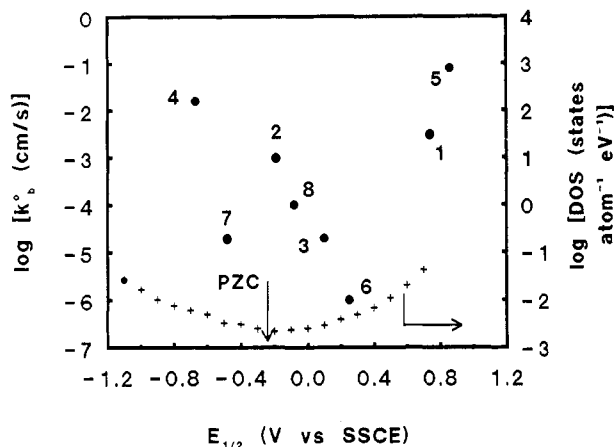(44) Gerischer, H. *J. Phys. Chem.* 1985, 89, 4249.

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Figure 5. Solids circles are validated basal plane HOPG rate constants (log $k_b{}^0$) plotted versus $E_{1/2}$ (defined in text) for systems involving one-electron transfers. Corresponding data and number assignments from Table II. Crosses are the DOS for HOPG, from ref 45.

gold (0.28 states atom^{-1} eV^{-1}).[46] The trend in the DOS calculated by Gerischer et al. from capacitance data for HOPG is shown in Figure 5 for comparison. Note that the variation in $k_b{}^0$ with $E_{1/2}$ does not track the DOS in any obvious way.

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Although the low DOS for HOPG may be a factor in depressing $k_b{}^0$ compared to $k_{GC}{}^0$, the dependence of $k_b{}^0$ on redox system $E_{1/2}$ is not that predicted if the DOS is the only important factor.

CONCLUSIONS

The 13 redox systems exhibit a wide range of electron-transfer rates on the basal plane of HOPG, but all are slower on basal plane graphite than on GC. Although the magnitudes of the differences in rate between GC and HOPG are somewhat uncertain due to residual defects, it is clear that rates on basal plane HOPG are 1–5 orders of magnitude lower than those on GC. The results permit identification of at least three major factors affecting electron transfer at carbon: charge-transfer mechanisms which are promoted by edge plane (e.g. those involving proton transfer), physico-chemical properties of basal plane which retard electron transfer (e.g. low density of electronic states), and the homogeneous self-exchange rate of the redox system involved. One or more of these effects can lead to major differences in observed rates for different carbon electrode materials and surface pretreatments. By continuing to examine both ordered graphite and GC surfaces, we intend to characterize these major factors affecting observed rates on carbon electrodes more completely, with the long-range goal of providing a structural basis for electron-transfer reactivity.

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