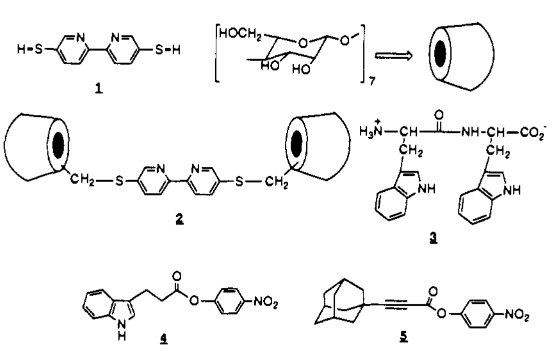

	k_{cat}	k_{un}	k_{cat}/k_{un}	k_{cat}	k_{un}	k_{cat}/k_{un}
pH 8.0	1.0×10^{-3}	1.0×10^{-7}	10^4	1.2×10^{-2}	1.8×10^{-7}	7×10^4
pH 7.0	0.55×10^{-3}	3×10^{-8}	1.8×10^4	0.68×10^{-2}	3×10^{-8}	2.2×10^5

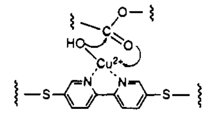

Figure 1.

Dithiol **1** was prepared by coupling of 3-methylpyridine to the bipyridine, conversion of the methyl groups to carboxyl and then amino, double diazotization, and reaction of the diazonium compound with potassium ethylxanthate. The resulting bis-dithiocarbonate was hydrolyzed and converted to the bis-thioacetate, and this was directly deprotected with NH_3 to the dianion of the dithiol **1** and used in the next reaction.

Reaction of the above dithiolate with β-cyclodextrin 6-iodide in DMF at 60–65 °C for 3 h afforded the cyclodextrin dimer **2** in 46% yield; it was isolated by reversed-phase chromatography and characterized by TLC, ^1H NMR, and FAB-MS (M + 1 = 2455). As expected, in water it was able to bind substrates having two appropriate hydrophobic groups. For instance, Trp-Trp **3** binds to **2** with an association constant of $(2.5 \pm 0.5) \times 10^6$ M^{-1}, raised 10-fold when Zn^{2+} is also bound to **2**.

The most striking property of **2** is the ability of some of its metal complexes to catalyze hydrolysis reactions of bound substrates. All reactions were performed in water at pH 7.0 or 8.0 and 37 °C, in contrast to many enzyme model studies that use extreme conditions. The k values (s^{-1}) shown in Figure 1 are the average of at least two runs, with good agreement.[6] Substrate **4** showed a rate enhancement for hydrolysis of over 10^4 (pH 7.0) with the Cu^{2+} complex of dimer **2** and of 80-fold without the Cu^{2+}. With simple β-cyclodextrin, the hydrolysis rate of **4** increased by a factor of only 30-fold, with and without Cu^{2+}.

With Cu^{2+} the data for rate vs pH and vs catalyst concentration fit a mechanism[8] in which the substrate binds to the Cu^{2+}/**2** catalyst, with $K_f = 7.0 \times 10^4$ M^{-1}, and is attacked by hydroxide bound to copper, from a bound water with $pK_a = 7.15$. Thus the observed acceleration relative to the simple hydroxide cleavage rate is at a maximum near pH 7. Ester **5** at 6.0×10^{-5} M shows a rate of hydrolysis with 1.0×10^{-4} M **2** and 2.0×10^{-4} M $CuCl_2$ at pH 7.0 and 37 °C that is 220 000-fold faster than the rate of uncatalyzed hydrolysis. The k_{cat} values are comparable in magnitude to those for the acylation step of one of the best catalytic antibodies by similar nitrophenyl esters.[9]

The nitrophenol and the corresponding carboxylic acid from **5** were both identified in approximately equal amounts by gas chromatography after isolation from the reaction catalyzed by Cu^{2+}/**2**. Furthermore, with an excess of substrate **5**, at least 50 turnovers were seen in the hydrolysis process. In our normal reactions the concentration of **5** is only 60% that needed (1.0×10^{-4} M) for solubility saturation, although in the turnover experiments it was 50 times higher and **5** was partially out of solution until the end of the hydrolysis reaction.

Thus, as hoped, stretching a substrate across a metal catalytic group has led to significant catalysis. We expect that the well-defined geometry in enzyme models using cyclodextrin dimers will lead to other advantages as well.

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(6) The least reliable are the values of k_{un} for pH 7.0, where the rates are extremely slow. However, the k_{un}'s at pH 8.0 are better defined, and those listed for pH 7.0 are if anything a little higher than expected for a reaction first order in OH^-. We have found previously[7] that the hydrolysis of *5* shows catalysis by buffer as well as by OH^-.

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Covalent Modification of Carbon Surfaces by Grafting of Functionalized Aryl Radicals Produced from Electrochemical Reduction of Diazonium Salts

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Modification of carbon surfaces is of interest to several fields of material science and electrochemistry. Probably most important from the industrial point of view is the modification of the surface of carbon fibers to improve the mechanical properties of composites, particularly carbon–epoxy composites.[1] Modification of electrode surfaces for catalytic or analytical purposes and biotechnological applications also currently attracts considerable attention.[2-8] Most of the available methods for modifying carbon surfaces involve their oxidation,[9-14] thus leading to the generation of superficial carboxylic, quinonic, ketonic, or hydroxylic groups[2] that are further reacted with the substance to be attached. The exact nature and number of oxygenated functional groups thus formed are difficult to ascertain and control, and corrosion of the carbon surface is often observed[15-17] leading to large background

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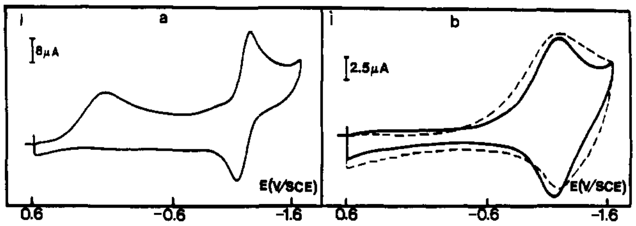

Figure 1. Cyclic voltammetry in ACN + 0.1 M NBu_4BF_4 on a GC electrode (v = 0.2 V s^{-1}, T = 22 °C) of **1** (a) (c = 0.7 mM) and of a derivatized electrode (b) after grafting (—) and after 6 months (- - -).

currents in electrochemical applications. It would therefore be desirable to develop alternative strategies for modifying carbon surfaces.[18]

For this purpose we have investigated a reductive, rather than an oxidative, strategy. It is based on the electrochemical reduction of diazonium salts, which leads to a very solid and noncorrosive covalent attachment of aryl groups onto the carbon surface.[19] The versatility of the method is founded on the possibility of grafting a large variety of functionalized aryl groups, hence allowing the attachment of a broad spectrum of substances.

(4-Nitrophenyl)diazonium tetrafluoroborate **1** in acetonitrile (ACN + 0.1 M NBu_4BF_4) gives rise on a (clean, carefully polished with 1 μm diamond paste) glassy carbon (GC) electrode to a broad (peak width: 180 mV), irreversible wave located at −0.04 V/SCE. This first wave is followed by the reversible wave of nitrobenzene ($E°$ = −1.18 V/SCE) that is formed upon reductive cleavage of **1** (Figure 1). At concentrations higher than 0.5 mM, the first wave of **1** shows the characteristics of an adsorption wave. On a second scan the first wave of **1** vanishes. Upon electrolysis at a GC cathode of a 1 mM solution of **1** for about 10 min and successive transfer to a pure supporting electrolyte solution, a single broad symmetrical signal is observed at the same potential as that of nitrobenzene (Figure 1). The signal is also very persistent with time: no change could be detected with electrodes left on a laboratory bench for several months (Figure 1) or with electrodes exposed to vigorous ultrasonic cleaning in ethanol, dimethylformamide, benzene, benzonitrile, and trichloroethane. The same observations were made with carbon fibers, carbon powder, or highly oriented pyrolytic graphite (HOPG) (basal plane or edge) electrodes. These experiments point to a strong covalent bonding of the 4-nitrophenyl group on the carbon surface rather than to mere adsorption. The grafting of the 4-nitrophenyl group was also investigated by XPS of GC plates. In agreement with cyclic voltammetry, these measurements indicate that the diazonium salt is adsorbed on the glassy carbon surface: after the GC plate is dipped in the solution and rinsed, signals are observed at 402 and 406 eV corresponding to the diazonium and nitro groups on the surface, respectively, and amounting to 1% of the overall signal. The intensity of the 406 eV signal increases to 7.3% after electrolysis and ultrasonic cleaning while the signal at 402 eV disappears.

The surface coverage of the modifying layer could be estimated through the integration of the voltammetric signal of the 4-nitrophenyl group. The effective surface area of the GC electrode was measured by adsorption of methylene blue and comparison with a mercury electrode of known surface. From these measurements, it appears that the surface coverage can be controlled through the concentration of the substrate and the electrolysis time. At a diazonium concentration of 1 mM and electrolysis times shorter than about 4 min, the surface coverage is a function of the time, with a limiting coverage being obtained for longer times. A very compact layer can be obtained for a 5 mM concentration of the diazonium salt: the surface is nearly completely covered by a close-packed monolayer of 4-nitrophenyl groups ($\Gamma = 14 \times 10^{-10}$ mol/cm^2).

The grafting of many other diazonium salts bearing different functionalities (for example, 4-cyano, 4-carboxy, 4-benzoyl, 4-bromo, 4-(carboxymethyl), 4-acetamidobenzene, and 4-nitronaphthalene) could also be achieved and observed by cyclic voltammetry and/or XPS.

Once attached to the carbon surface, the functionalized aromatic groups could be modified by classical chemical reactions. For example the 4-nitrophenyl group obtained from **1** could be reduced electrochemically (in 10/90 $EtOH/H_2O$ + 0.1 M KCl, irreversible 6e peak) to a 4-aminophenyl group (the CV and XPS signals of the nitro groups disappear and the XPS signal of the amino group appears). Such an amino group could also be obtained by hydrolysis of a 4-acetamidophenyl group. This 4-aminophenyl group could in turn be reacted with an epoxy function such as that of epichlorohydrin (the chlorine atom can be observed by XPS), demonstrating the possibility of generating covalent bonds between the carbon surface and epoxy resins. Preliminary experiments also indicated the viability of the attachment of enzymes along a similar strategy.[20]

We assign the covalent attachment of the aryl groups to the binding of the aryl radical produced upon one-electron reduction of the diazonium salt to the carbon surface. Two factors favor such a reaction: (i) the diazonium salt is adsorbed prior to its reduction, and (ii) the aryl radical is not reduced at the very positive reduction potential of the diazonium salt (opposite to what is observed, for example, with aryl halides). As concerns the carbon surface, the covalent binding seems to involve at the same time edge defects and polycyclic aromatics, as shown by the attachment of aryl groups to the basal plane of HOPG.

As a result of the reductive strategy we used and of the strong bonding between the surface and the aryl groups, low residual currents (similar to those observed at a bare electrode) were obtained over a large window of potentials, the same as for the unmodified parent GC electrode.

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Superacid-Catalyzed Protium–Deuterium Exchange in Isobutane Competing with *tert*-Butyl Cation Formation

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That saturated hydrocarbons do react at room temperature and below with various superacidic media[1] has been known since the late 1960s when Hogeveen[2] and Olah and his group published their pioneering work. Both Hogeveen[4] and Olah,[5] in a HF–SbF_5–Freon

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