alcohols; this difference is traditionally assigned to cooperative inductive (s-character of carbon) and mesomeric (charge delocalization) effects, both of which should indeed come to play a second time in going from enols to ynols.

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Electrical Communication between Redox Centers of Glucose Oxidase and Electrodes via Electrostatically and Covalently Bound Redox Polymers

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Electrical communication between redox centers of enzymes and metal electrodes is of essence in amperometric biosensors and in electrodes for selective electrosynthesis of biochemicals. Direct electrical communication between the centers and electrodes is prevented by thick insulating protein layers that surround the centers. Thus, for example, the two $FADH_2$ redox centers of reduced glucose oxidase [E.C. 1.1.3.4] are prevented from transferring electrons to metal electrodes by an insulating glycoprotein shell. Transfer of electrons has, nevertheless, been effectively mediated by low molecular weight, fast redox couples that diffuse into and out the enzyme. Mediators employed in amperometric glucose sensors include ferrocenes,[1a] quinones,[1b] components of organic metals,[1c] octacyanotungstates,[1d] and ruthenium complexes.[1e] Recently, direct, unmediated electrical communication has been established between electrodes and glucose oxidase to which electron relays were covalently or coordinately bound.[2]

Here we show that the redox centers of glucose oxidase can be readily electrooxidized via a high molecular weight (MW ~ 60 000) polycationic redox polymer. The polymer forms an electrostatic complex with the polyanionic enzyme, wherein the electron-transfer distance is reduced (Figure 1a). The complex forms at low ionic strength, where the polycation is "stretched" by internal electrostatic repulsion. At high ionic strength, screening

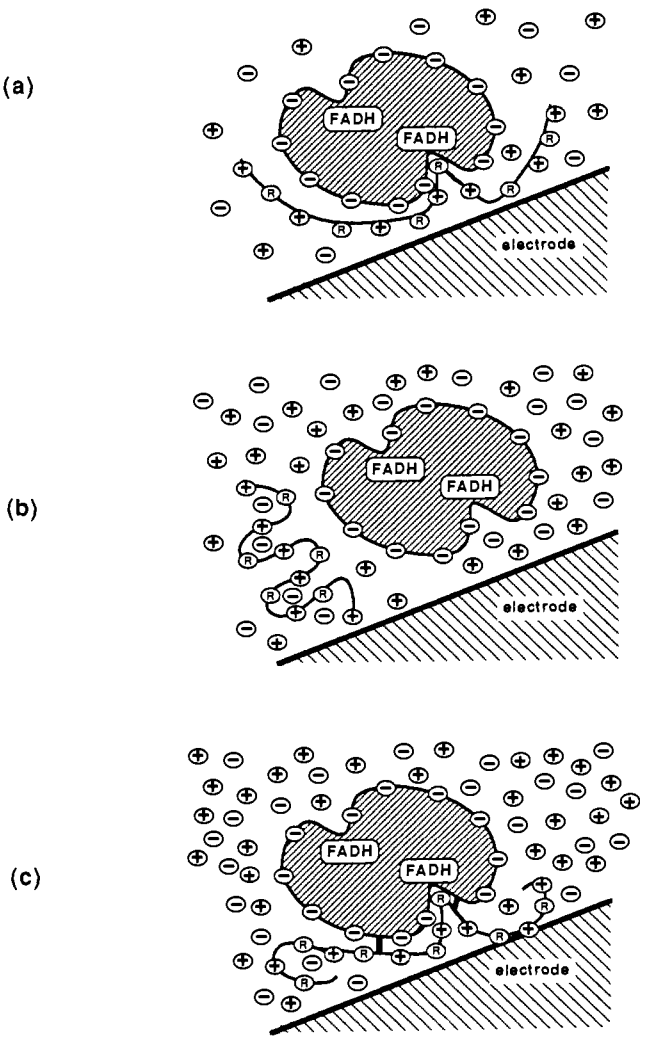

Figure 1. (a) Electrostatic bonding of a polycationic redox polymer to a polyanionic enzyme at low ionic strength brings redox centers of the two within range for electron transfer. Electrons are transferred to the electrode via the polymer. (b) Charge screening and coiling of the redox polymer at high ionic strength leads to dissociation of the electrostatic complex, stopping electron transfer, and thereby electrooxidation of glucose. (c) After covalent bonding of the redox polymer to the enzyme, the complex does not dissociate at high ionic strength, and electrooxidation of glucose persists.

of the polymer and enzyme charges by counterions and probably coiling of the polymer (through bonding of pairs of cationic sites to an anion) prevent formation of the complex[3] and electron transfer does not take place (Figure 1b). The redox polymer enzyme complex is, however, preserved even at high ionic strength if the polymer is covalently bound to the enzyme. Upon such bonding, the electrooxidation of glucose persists even at high ionic strength (Figure 1c).

The two polymers employed in this study were (1) a copolymer of poly(*N*-methylvinylpyridinium chloride) and of poly(vinylpyridine $Os(bpy)_2Cl$) and (2) the same with ~1/20th of the vinylpyridine/pyridinium replaced by 4-aminostyrene. Diazoti-

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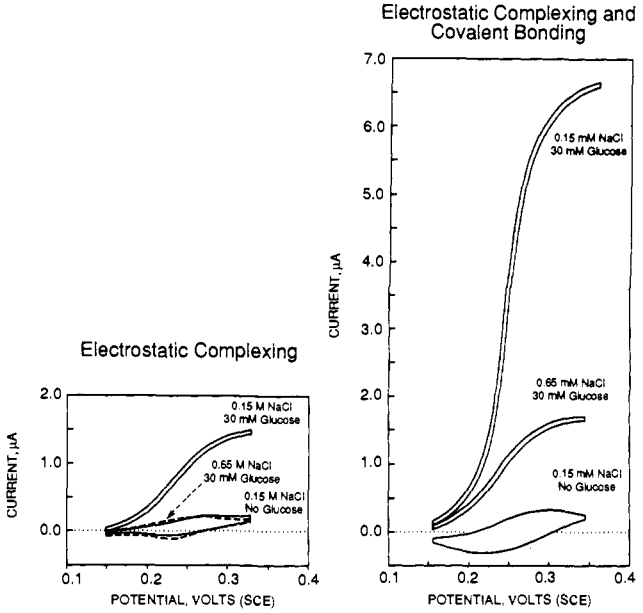

Figure 2. Cyclic voltammograms for glucose oxidase enzyme electrodes: Without glucose, 0.15 M NaCl; with 30 mM glucose, 0.15 M NaCl; and with 30 mM glucose, 0.65 M NaCl. Left: enzyme electrodes made with the copolymer of poly(vinylpyridine $Os(bpy)_2Cl$) and poly(vinyl-*N*-methylpyridinium chloride). Right: enzyme electrode made with the same polycationic redox polymer but covalently bound to the enzyme's tyrosine functions through azo links. 3 mm diameter glassy carbon electrodes; scan rates 2 mV/s.

zation of the copolymerized aminostyrene followed by reacting the diazonium salt with tyrosine functions of the enzyme allows covalent bonding of the redox polymer to hydrophilic channels in the enzyme's protein.

Cyclic voltammograms of the resulting enzyme electrodes are shown in Figure 2. Glucose is electrooxidized at moderate ionic strength (0.15 M NaCl), where the first (i.e., not covalently bound) redox polymer is electrostatically complexed to the enzyme but not at high ionic strength (0.65 M NaCl) where the electrostatic complex dissociates (Figure 2, left). When the redox polymer is covalently bound to the enzyme (Figure 2, right), a high glucose oxidation current is observed at low ionic strength that persists at high ionic strength. At 0.65 M NaCl the glucose electrooxidation current for the covalently bound system is as high as for the electrostatic complex at 0.15 M NaCl.

Because glucose oxidase is itself a polyelectrolyte, the loss of current at 0.65 M NaCl could be caused simply by structural changes in the enzyme. We find, however, that enzyme-related changes account only for a minor fraction of the loss. To test for these changes we measured the output of glucose electrodes made with glucose oxidase and low-molecular weight redox mediators, either neutral (ferricinium carboxylate) or positively charged (protonated dimethylaminomethylferricinium chloride) at different NaCl concentrations. Upon increasing the NaCl concentration from 0.15 to 0.65 M the currents of the two electrodes (at +0.45 V vs SCE) declined only by 20% and 30%, respectively, in contrast with the current of the electrode made with the polycationic redox polymer that dropped by a factor of >50 essentially to nil (Figure 2, left). We conclude that it is primarily the breakup of the electrostatic complex between the redox polymer and the enzyme, not a structural change in the enzyme, that causes the drastic decline in the glucose-dependent current at high ionic strength.

Electrostatic complexing of oxidoreductases and redox proteins, whereby electron transfer becomes possible, is known for the cytochrome *c* peroxidase/cytochrome *c* system, for the cytochrome *c* oxidase/cytochrome *c* system, and for the ferredoxin $NADP^+$ oxidase/ferredoxin system. These natural electron-transfer complexes, like the synthetic ones described here, are sensitive to ionic strength before, but not after, covalent attachment of the redox proteins to their complexing enzymes.[4]

The significance of low molecular weight organic nitrogen compounds in promoting electron transfer between electrodes and the smaller redox proteins, like cytochrome *c* (but not between electrodes and the larger redox enzymes) is well documented.[5] We see here that adsorption of a polycationic redox polymer on an electrode and its interaction with glucose oxidase also enhance electron transfer and form the basis of a glucose electrode.

In summary, we find that the natural process of electron transfer in electrostatic complexes between polyanionic enzymes and polycationic redox proteins can be mimicked: electron transfer takes place in a complex between polyanionic glucose oxidase and a polycationic redox polymer. The complex decomposes, and the electron-transfer rate becomes vanishingly small, at high ionic strengths. The rate of electron transfer remains, however, fast even at high ionic strengths if the redox polymer and the enzyme are covalently bound.

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Confinement Control in Solid-State Photochemistry[1]

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For three decades our research group has been investigating unusual photochemical organic reactions in solution. In recent years we have returned to these reactions and studied their counterpart crystalline photochemical reactivity. In view of the increasing interest[2] in this area, we wish to report our preliminary findings.

We report (1) three striking examples of control of photochemical rearrangements by crystalline environment, (2) quantum

(1) We have used "Photochemistry in a Box" informally to describe these studies.

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