etry and by a reference PE spectrum[46]. The UPS delivered an operational resolution of about 30 meV for the ${}^2P_{3/2}$ band of Ar$^+$. Experimental ionization energies were calibrated by the simultaneous addition of small amounts of Ar and CH$_3$I with the sample.

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The Kinetic Order of an Interfacial Diels–Alder Reaction Depends on the Environment of the Immobilized Dienophile[**]

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Substituent effects are used widely in physical organic chemistry to elucidate the relationships between the structures, reactivities, and properties of molecules. This mechanistic tool finds routine use in many areas, including the determination of reaction mechanisms,[1] the development of catalysts,[2] and the design of selective inhibitors of proteins.[3] We have a program to extend the principles of physical organic chemistry to the reactions of molecules confined at the solid–liquid interface in order to elucidate the factors that uniquely affect these reactions. Here we show one such effect wherein the reaction of an immobilized molecule is influenced by a substituent effect arising from the surrounding microenvironment. We use the Diels–Alder reaction of soluble cyclopentadiene with quinone immobilized to a self-assembled monolayer (SAM) on gold as a model system.

This work uses monolayers prepared from an alkanethiol terminated in a hydroquinone group and a second alkanethiol terminated in either a methyl or hydroxy group (Figure 1). The reversible two-electron electrochemical oxidation of this hydroquinone to the quinone is well known.[4] In previous work we showed that this quinone undergoes a Diels–Alder reaction with cyclopentadiene (Cp) dissolved in the electrolyte to give the cycloaddition adduct.[5] Since this adduct is not

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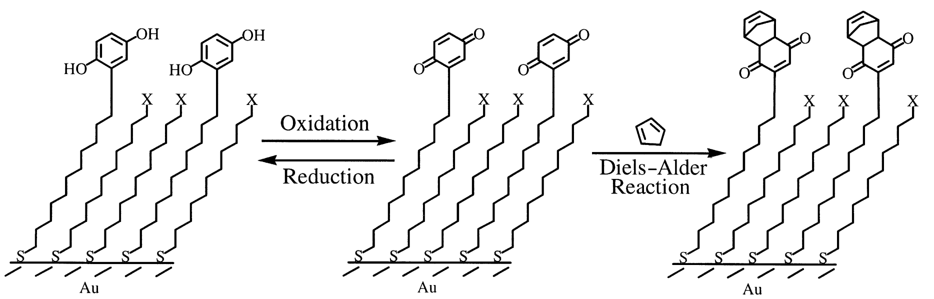

Figure 1. Reversible electrochemical oxidation of a monolayer that presents hydroquinone groups together with either methyl (X = CH_3) or hydroxy (X = OH) groups affords a monolayer that presents the quinone group. The resulting quinone reacts with cyclopentadiene to give the Diels – Alder adduct.

redox active, the rate of quinone loss, and hence the rate constant for the reaction, can be measured using cyclic voltammetry. Figure 2 a shows a set of consecutive cyclic voltammograms for a monolayer that presents quinone groups ($\chi_Q = 0.10$) and hydroxy groups in 1:1 tetrahydrofuran:water containing sodium phosphate (2 mM), sodium chloride (75 mM), and cyclopentadiene (15.2 mM).[6] Under these conditions the hydroquinone group undergoes oxidation at 220 mV (versus Ag/AgCl) and the resultant quinone group is reduced at −150 mV.[7] The waves for both oxidation and reduction decrease at the same rate over consecutive voltammograms. Several observations confirm that the decrease in the amount of quinone is due to the Diels – Alder reaction occurring. First, in the absence of cyclopentadiene the voltammograms showed no change over 100 cycles. Second, the use of the structurally related molecules cyclopentane and cyclopentene resulted in no change in the voltammograms over as many cycles. Third, a comparison of grazing angle IR spectra of the monolayers before and after reaction are consistent with the expected product of the Diels – Alder reaction (Figure 2 b). Monolayers presenting only quinone groups showed an absorption band at 1663 cm^{-1} in the IR spectra, which corresponds to a carbonyl stretch of the quinone molecules.[8] After this monolayer was exhaustively treated with cyclopentadiene a new band appeared at 1652 cm^{-1}, which corresponds to the carbonyl stretch of the Diels – Alder adduct. The shift of the carbonyl stretch by approximately 10 cm^{-1} has been reported for the reaction of quinone and cyclopentadiene in solution.[9] Fourth, ellipsometry showed that the thickness of the monolayer increased by the expected amount following reaction with 1-hexylcyclopentadiene.[10] Finally, this reaction has been used to immobilize ligands for the biospecific recognition of proteins.[5]

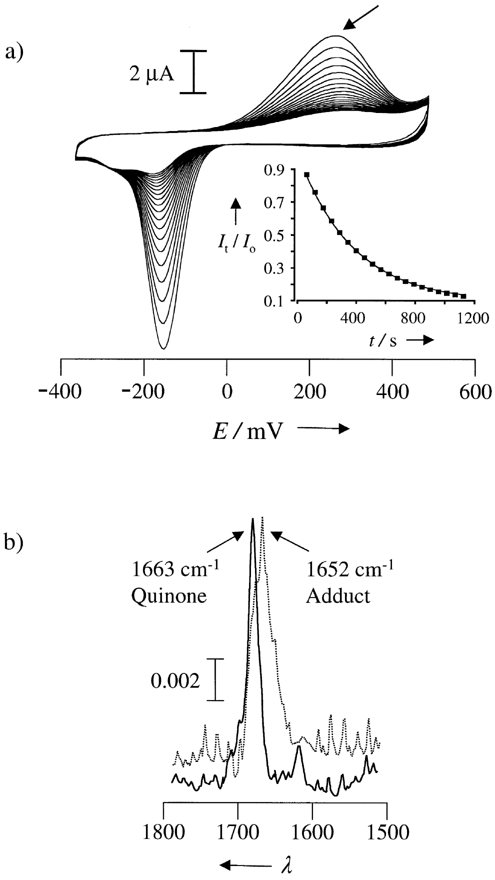

Figure 2. a) Consecutive cyclic voltammograms of a monolayer presenting hydroquinone groups ($\chi_Q = 0.10$) and hydroxy groups at a scan rate of 25 $mV s^{-1}$ versus the Ag/AgCl reference electrode. The arrow denotes the first scan. Inset: A plot of the peak current showing the reduction in the amount of immobilized quinone versus time. See text for further information. b) Grazing-angle infrared spectra of the carbonyl stretching region of a monolayer presenting quinone groups prior (solid line) and after complete reaction with cyclopentadiene (dashed line). The two spectra are offset slightly for clarity and have intensities given by the scale bar.

To determine the rate constant for the Diels – Alder reaction we analyzed the loss in peak current for the reduction of quinone over consecutive cyclic voltammograms (inset Figure 2 a).[11] Since the concentration of cyclopentadiene was much greater than that of immobilized quinone, the loss in peak current could be fit to an exponential decay [Eq. (1)] to obtain a pseudo first-order rate constant k'.

$$I_t = I_f + (I_o - I_f)\exp^{-k't} \qquad (1)$$

I_t is the peak current at time t, I_o is the initial peak current, and I_f is the residual nonfaradaic current. The excellent fit of the experimental data with this equation indicates that the reactivity of the quinone groups is homogeneous and independent of the extent of the reaction. We repeated this experiment using different concentrations of cyclopentadiene, and in all cases found the reaction proceeded with homogeneous first-order kinetics and to completion for monolayers with quinone ($\chi_Q = 0.10$) and hydroxy groups. The pseudo first-order rate constants increased linearly with the concentration of cyclopentadiene (0.76 – 58 mM). The slope of the best-fit line to these data provided a second-order rate constant of $k_{DA} = 0.26 M^{-1} s^{-1}$, after correction for the fraction of time that quinone was present (Figure 3 a). This rate constant was independent of the density of quinone over the range $\chi_Q = 0.1 – 0.5$ and shows that the reactivity of the immobilized quinone was not affected by lateral interactions with neighboring quinones molecules on the monolayer.[12]

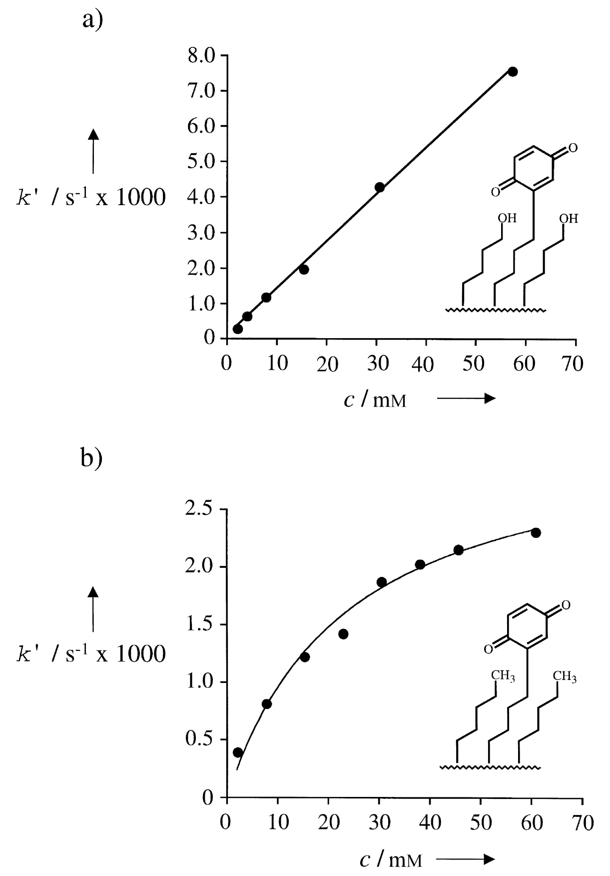

Figure 3. A comparison of the kinetic behavior for the reaction of cyclopentadiene with monolayers presenting quinone groups mixed with hydroxy groups (a) or with methyl groups (b). See the text for an explanation of the best fit curve in (b).

We next repeated these experiments for monolayers that presented quinone groups surrounded by methyl groups ($\chi_Q = 0.10$). All experimental conditions were identical to those described above and we again found, for all concentrations of cyclopentadiene, that the reaction proceeded with homogeneous first-order kinetics and to completion. A comparison of the first-order rate constants with the concentration of cyclopentadiene showed that they were not linearly related (Figure 3b). Instead, the first-order rate constant reached a limiting value with higher concentrations of cyclopentadiene. Since this kinetic behavior is inconsistent with a bimolecular reaction, we reasoned that the diene might first adsorb onto the monolayer and subsequently react with an immobilized quinone moiety.[13] In this scheme the reaction of quinone with adsorbed diene is effectively intramolecular, and hence should proceed with apparent first-order kinetics. The overall rate is then the product of the first-order rate constant (k_{rxn}), the surface concentration of quinone (Γ_Q), and the fraction of available quinone sites on the monolayer to which cyclopentadiene is adsorbed [Eq. (2), θ is the fractional coverage and varies between 0 and 1].

$$\text{rate} = k_{rxn}\theta\Gamma_Q \qquad (2)$$

We used a Langmuir isotherm to relate θ to the concentration of cyclopentadiene, and the association constant for the adsorption of diene onto the monolayer (K_{ads}). This relation makes the assumption that adsorption is reversible, at equilibrium, and that the energy of association of a molecule at a given site is independent of the adsorption of a second molecule at a neighboring site. The data relating the first-order rate constant (k') and the concentration of diene were fit to Equation (3) with k_{rxn} and K_{ads} as adjustable parameters. The fit was excellent and gave values for K_{ads} and k_{rxn} of 41.0 M^{-1} and 0.0032 s^{-1}, respectively (Figure 3b).

$$k' = \frac{k_{rxn} K_{ads}\,[\text{Cp}]}{1 + K_{ads}\,[\text{Cp}]} \qquad (3)$$

This work provides a dramatic example of the extent to which a change in the microenvironment of an immobilized group can affect the kinetic course of a reaction of that group with a soluble reactant. The second-order rate constant observed when quinone was surrounded with hydroxy groups is consistent with a bimolecular reaction of these two groups in a manner analogous to that for the same reaction in solution. The kinetic pathway changes completely on changing to an environment of methyl groups. We believe that the data are most consistent with an equilibrium adsorption of diene onto the monolayer followed by a first-order reaction of the two molecules. The velocity of the second-order reaction on monolayers presenting hydroxy groups is faster than the first-order reaction for monolayers presenting methyl groups. Even so, the second-order bimolecular reaction does not compete with the slower first-order process on monolayers that present methyl groups. This second-order pathway apparently is not inhibited by association of cyclopentadiene with the SAM, since low concentrations of cyclopentadiene (which give small θ, and hence leave many quinone groups uninhibited) display only the first-order pathway. The partitioning of the reaction between these two pathways therefore depends not only on the equilibrium adsorption constant (K_{ads}) of the diene with the monolayer, but also on the structure and solvation of the interface. We are currently exploring the effects that several other parameters have on this partitioning, including composition of the solvent, structure of the diene, identity of the functional groups surrounding the quinone, and the conformational flexibility of the tether connecting the quinone to the monolayer.

The use of SAMs and electrochemistry were essential to the studies described here. SAMs are structurally well-defined surfaces that permit wide flexibility in tailoring the environments of reactive groups and in controlling the densities of these groups. The use of cyclic voltammetry—and the related choice of a reactant that displays a reversible redox couple—permitted measurement of the rate of reaction with a resolution on the order of tens of seconds. The combination of techniques described here—SAMs and electrochemistry—provides an effective model system for physical organic studies of interfacial reactions[14] and will be important to elucidating other factors that are unique to reactions at surfaces.

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[6] χ_Q is the fraction of alkanethiolates in the monolayer that present quinone groups, and was determined by integrating the waves in the cyclic voltammograms.

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[12] A monolayer presenting only quinone groups gave heterogeneous kinetic behavior in that the reactivity of the quinone groups was dependent on the extent of reaction. This contrasting behavior gives evidence that the mixed monolayers used in this work were not phase-separated.

[13] This model is analogous, though not identical, to the formalism of Langmuir–Hinshelwood. For a review, see W. H. Weinberg, *Acc. Chem. Res.* **1996**, *29*, 479.

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Highly Efficient Phosphapalladacyclic Catalysts for the Hydroarylation of Norbornene

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In the last decade, organopalladium-catalyzed C–C bond formation has become one of the most important tools in the synthesis of organic molecules.[1] In particular, the Heck reaction is an important method for the preparation of aryl-functionalized alkenes in synthetic chemistry and the pharmaceutical industry.[2] Attempts to achieve industrial-scale application of this reaction proved difficult due to the need for relatively large amounts of palladium catalysts and/or expensive aryl iodides. The former problem can be overcome by more efficiently recycling the catalyst, and the latter by using catalysts of higher activity or by activating the cheaper aryl bromides and chlorides. Herrmann, Beller et al.[3] and Milstein et al.[4] described recently the synthesis of phosphapalladacycles and their use as efficient catalysts for the Heck reaction that give turnover numbers (TON)[5] one to three orders of magnitude higher than those reported before ($\text{TON} > 100000$). Cyclopalladated complexes, formed in situ from mixtures of Pd^{II} salts and tri-*o*-tolylphosphane were investigated.[6] More recently, it was found that fine tuning of the phosphorus ligand sphere could improve these results, and chelating diphosphanes containing P–N bonds gave higher turnover values ($\text{TON} > 200000$).[7] In recent years, we have studied and developed the potential of oxazaphospholidine and diazaphospholidine ligands in various catalytic reactions.[8–10] Systems in which the phosphorus atom is substituted by two nitrogen and one oxygen atom or one aromatic carbon atom proved to be excellent mediators for, inter alia, highly selective allylic substitutions,[8] copper-catalyzed Diels–Alder reactions,[9] and asymmetric cyclopropanations.[10] Here we report the synthesis of a new class of bis(alkylamino)-*p*-tolylphosphane ligands and their high efficiency in the palladium-catalyzed hydroarylation of norbornene and norbornadiene; they surpass all previously known catalysts as regards stability, lifetime, and turnover frequency (TOF).[5]

The synthesis of bis(dimethylamino)-*o*-tolylphosphane (**1**) was achieved in 78% yield from *o*-tolylmagnesium bromide and chloro-bis(dimethylamino)phosphane in THF at 0°C (Scheme 1). Ligands **2** and **3** were synthesized from **1** by exchange reaction in refluxing toluene with two equivalents of the corresponding amine in 76 and 58% yield, respectively (Table 1).[11]

Treating palladium(II) acetate with **1**–**3** in refluxing toluene gave the expected palladacyclic complexes **4a**–**c** in high yields (90–95%) as thermally stable yellow solids insensitive to air and moisture (Scheme 2). The cyclometallated structure

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