In preliminary work we have observed an enhancement of the Chl *a* water photolysis rate on addition of an equimolar amount of β-carotene in the Pt/Chl *a* sample. Independent identification of these products by gas chromatography and microwave spectroscopy are underway. Recently Somorjai et al.[23] described the UV-light-assisted photosynthesis reaction of CO_2 and H_2O adsorbed on $SrTiO_3$ crystals in contact with Pt foils. The visible-light photosynthesis reaction described in this work is relevant to the current interest in solar conversion and energy storage.[24]

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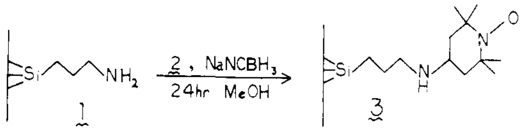
A Method for Determining the Spatial Distribution of Spin-Labeled Organic Ligands Covalently Bound to a Noncrystalline Surface: Dipolar Contribution to Nitroxide EPR Spectrum

Sir:

There is a considerable current interest in the chemistry of organic ligands covalently attached to noncrystalline surfaces. Consequently there is a need for the development of methods for the chemical characterization of these modified surfaces. Where it is necessary to determine merely the composition or structure of the surface-bound ligands, techniques such as Auger, ESCA, EPR, laser Raman, and IR spectroscopy may be useful; however none of these has been used to determine the distribution of ligands on a noncrystalline surface.[1] In addition, with most of these techniques, the bulk substance is not transparent; so application to porous materials is impossible. The design of any experiment in which it is desired to prevent the interaction between ligands covalently bound to an organic polymer or an inorganic surface requires that the ligand distribution be known or assumed.[2] We report here that the contribution from dipolar coupling to the EPR line width from a nitroxide spin-labeled organic ligand, measured under conditions where molecular motion is slow, can give ligand–ligand distances and distributions on a modified silica surface.[3]

Controlled-Pore glass,[4] a commercially available amorphous inorganic support composed of microporous 96% silica, was derivatized with 3-aminopropyl ligands by absorption from degassed aqueous alkaline solutions of freshly hydrolyzed 3-aminopropyltrimethoxysilane followed by drying and curing[5] to yield[6] **1**. Samples of **1** having different surface concentrations[7] of ligand, ρ_{NH_2}, were prepared. It was not possible to bind more organic ligand to the surface than would be required to form one molecular layer; the highest ρ_{NH_2} obtained was 3.9 ± 0.2 nm^{-2}.

Spin labeling of **1** was achieved by reductive alkylation using an excess of 2,2,6,6-tetramethyl-4-oxopiperidine-1-oxyl (**2**) with sodium cyanoborohydride in methanol. The spin-labeled product, **3**, after washing, gave an EPR spectrum characteristic of a partially immobilized nitroxide. Release of mobile nitroxide was seen only under conditions which caused the dissolution of the silica surface itself (e.g., immersion in 0.1 M NaOH); in contrast the Schiff base analogue of **3**, prepared analogously omitting the cyanoborohydride, hydrolyzed readily under mild aqueous conditions liberating mobile nitroxide. From these and other observations, it was established that **3** had the structure shown. That each 3-aminopropyl group was indeed covalently bonded to the surface will be shown below.



The surface density of nitroxides, ρ_{SL}, was determined by EPR double integration. Within the accuracy of determination

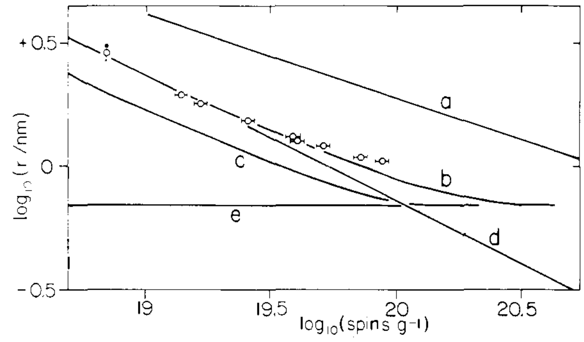


Figure 1. Plot of EPR double integral vs. mean nearest-neighbor distance $\bar{r}$ (obtained from dipolar broadening) for **3** under methanol at 77 K. The theoretical curves a-e are discussed in the text. The error bars indicate the precision of measurement of d_1/d and the double integrals.

of ρ_{NH_2}, it was found that, when ρ_{NH_2} was low, monoalkylation was complete. However, when ρ_{NH_2} was high, monoalkylation was incomplete based on **1**; the maximum ρ_{SL} obtained, 1.5 nm^{-2}, was consistent with a single molecular layer of nitroxide moieties close packed in two dimensions.

There are a number of possible methods for determining spin-spin distances. If the orientations of the spin-spin vectors are random with respect to the magnetic field and the rates of molecular reorientation and electron and ^{14}N spin-lattice relaxation are slow, the contribution to the line width from dipolar coupling is a function of the microscopic spin-spin distances. If the spins are dilute, this dipolar broadening arises almost entirely from nearest-neighbor couplings. On the other hand, trivially, the EPR double integral is a macroscopic quantity dependent only upon the average ligand density and independent of the spatial distribution. Thus, a comparison of nearest-neighbor distances (obtained from dipolar broadening) with the EPR double integral should indicate whether the ligand distribution deviates from randomness.[8]

The spectral parameter[9] d_1/d was used as a measure of dipolar broadening. It is a linear function both of the intrinsic line width (i.e., that part not due to A and g anisotropy) and of the concentration of homogeneous frozen methanol solutions of **2** below 250 mmol L^{-1}. From the latter dependence, the relationship between d_1/d and $\bar{r}$, the mean nearest-neighbor distance, was found.

In Figure 1 is shown a plot[10] for **3** under methanol of $\bar{r}$ (obtained from d_1/d at 77 K) against the EPR double integral. The theoretical curves represent (a) spins randomly distributed in three dimensions throughout the entire pore volume (0.65 mL g^{-1}) of the sample; (b) spins, associated with an effective molecular area[11] of 0.5 nm^2, randomly distributed over the entire measured surface area (2.17 × 10^{20} nm^2 g^{-1}); (c) same as (b), but only half the surface was available for spin labeling; (d) same as (b), but nitroxides have zero molecular area; (e) spins, having an effective molecular area of 0.5 nm^2, distributed in patches of closely packed ligand. Clearly hypothesis b, random two-dimensional distribution with correlation by molecular volume, agrees well with the data. The deviation from (b) at high ρ_{SL} probably arises from our neglect of non-nearest-neighbor dipolar couplings (there are proportionally more of these in three than in two dimensions). Since this deviation is in the direction of high $\bar{r}$, it is unlikely to reflect a deviation from randomness. Hypothesis e, which corresponds, for example, to a model in which the 3-aminopropyl ligands do not bind covalently to the surface but exist in patches of tightly adsorbed oligosiloxane so that d_1/d is insensitive to ρ_{SL} is clearly excluded.

The high sensitivity of EPR spectroscopy, combined with the ready availability of methods for spin labeling a wide variety of organic functionality, promises to ensure that this technique has widespread applicability. Studies on other surfaces including cellulose and biological membranes are in progress in this laboratory.

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Sequential Oscillations in Mixed-Substrate Belousov-Zhabotinskii Systems

Sir:

The Belousov-Zhabotinskii (BZ) reaction[1] is the most thoroughly characterized of the known nonbiological oscillating chemical reactions.[2] A large number of organic substrates[3,4] have been found to give rise to oscillations when combined with appropriate metal catalysts and concentrations of bromate and sulfuric acid in the BZ reaction. Different substrates produce a considerable variation in such features

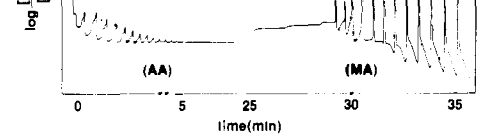

Figure 1. Oscillations in a mixed MA-AA system. Initial concentrations: [H_2SO_4], 0.93 M; [$KBrO_3$], 0.07 M; [$MnSO_4$], 0.017 M, [AA], 0.015 M; [MA], 0.035 M. Note the shoulders and color changes described in the text.