consistent with values observed for cycloadditions (25–40 cm^3 mol^{-1}).[21]

Because organic solvents possess large thermal expansivities, the reaction volume may only contribute a small fraction to the photoacoustic signal. One should be cautious, however, in interpreting enthalpies measured by PAC; if one does not explicitly account for the reaction volume, then the PAC measurement is only an estimate of the reaction enthalpy. By examining a reaction across the series of alkanes, PAC not only reliably determines the enthalpy of reaction but also yields the reaction volume and thereby provides insight into solvation phenomena.

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Supplementary Material Available: Table of solvent parameters α, MW, C_p, ρ, ϵ, and X_s and experimental values of f_h^{obsd} for DPCP measured against ferrocene and tetraphenylethylene at 337.1 nm (1 page). Ordering information is given on any current masthead page.

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(20) In aqueous mixtures, ΔV_{rxn} has been measured to be 63 ± 7 cm^3 mol^{-1} (ref 5). Theory predicts, however, that the volume associated with electrostriction around DPCP in water should be less than 1 cm^3 mol^{-1}, while the volume change due to fragmentation should remain the same as in alkanes (ref 17).

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Biradicals and Spin-Correlated Radical Pairs Anchored to SiO_2 Surfaces: Probing Diffusion at the Solid/Solution Interface

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Flexible organic biradicals continue to attract the attention of chemists, because of the special relationship between their spin mechanics, chain dynamics, and chemical reactivity.[1] The interplay of these properties makes an analysis of the electron paramagnetic resonance (EPR) spectra of biradicals complex, yet provides distinct advantages for the study of diffusional dynamics, particularly in cases of restricted diffusion. Recently there have been many reports of spectroscopic measurements on organic intermediates in contact with or bound to silica surfaces, by optical and steady-state EPR methods.[2] We have initiated a program aimed at measuring, using time-resolved EPR spectroscopy, the dynamic properties of flexible biradicals and radical pairs at interfaces. We report here the results of our initial experiments on acyl/alkyl biradicals and radical pairs (RPs) covalently bound to polycrystalline SiO_2 surfaces. In a separate paper, EPR results on surface-anchored, noninteracting monoradicals will be reported.[3]

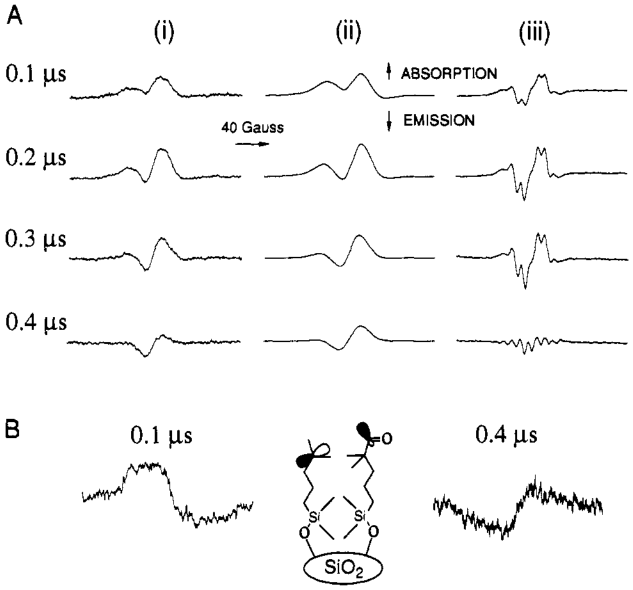
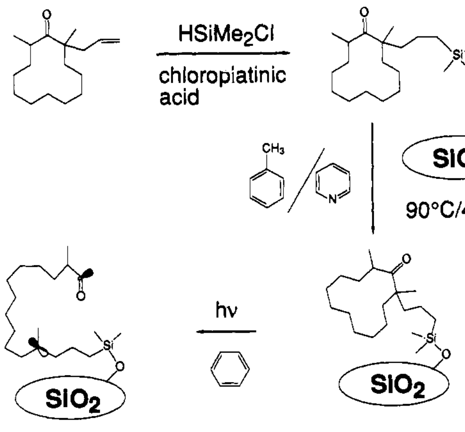


Figure 1. (A) (i) Time-resolved EPR spectra of surface-bound biradical **2** taken at the delay times shown at a temperature of 30 °C. All spectra are centered at 3385 G. Spectra taken at 0.1 µs are broadened due to instrument response. The intensities are normalized. (ii) Simulation using g(acyl) = 2.0008, g(alkyl) = 2.0025, a_H = 22.2 G (3 H), 17.8 G (4 H), LW = 22 ± 1 G, $k_{en} = 7.2 \pm 0.2 \times 10^{10}\ s^{-1}$, $J = -180 \pm 30$ MHz, initial populations of T^- = 0.35 and T^0 = 0.33. (iii) Spectra of the 1,12-acyl/alkyl biradical from the photolysis of a 0.084 M solution of 2,2,12,12-tetramethylcyclododecanone in benzene at 27 °C. (B) Spectra taken at the two delay times indicated for the spin-correlated radical pair shown. Experimental conditions and field axis scale are the same as in part A.

Scheme I



2 1

The surface attachment of precursor ketones was accomplished following literature procedures[4] which are summarized in Scheme I. Silicon oxide (PQ Corporation, BET surface area 366 m^2 g^{-1}) was treated by vacuum heating overnight before and after the

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attachment reaction was run. FTIR spectroscopy was used to confirm the presence of the ketone carbonyl stretch (1686 cm^{-1}) after the workup. Detection of the biradicals was accomplished by photolyzing a slurry of the modified silica in benzene (2 g of modified silica/100 mL of benzene) at 308 nm as the sample was pumped through a 1-mm quartz flat cell inside the cavity of a Varian E-9 X-band EPR spectrometer, which was equipped for direct detection as described previously[1b] except that the microwave bridge was modified to provide a faster time response.[5]

Direct detection EPR spectra of surface-bound biradical **2** produced by photolysis of ketone/silica system **1** are shown for several boxcar gate delay times in Figure 1A(i), and the simulated spectra, to be discussed below, are shown in Figure 1A(ii). These spectra are remarkably different from those from photolysis of a similar ketone in free solution, shown for comparison in Figure 1A(iii). For instance, the net absorption at early times is indicative of a strong triplet mechanism (TM) spin polarization, the first observation of this phenomenon in a mobile two-spin system.[6] The spectra also change shape much more drastically with time than do the solution spectra, and the line widths are clearly larger.

Simulation of the biradical spectra allows accurate determination of several important parameters: the initial populations of the triplet biradical spin states, the electronic spin–spin coupling J, and the encounter rate of the unpaired spins k_{en}. We make use of a well-established model for biradicals in solution.[7] The standard electronic basis set is employed: three triplet states (T^+, T^0, and T^-) which are nondegenerate in the applied field, and a singlet state (S) close in energy to at least one of the triplet levels and separated from T^0 by $|2J|$. Chemical reaction occurs only from the S state, which aquires a population from the triplet levels through nuclear hyperfine and spin–orbit coupling induced state mixing. The model is modified to account for the TM polarization passed on to the biradical from the parent ketone according to the model of Wong et al.[8] For the cycloalkanones used in this work, the TM will produce a net absorption.[9] Our simulation program stipulates that the initial triplet populations should sum to unity, and we let two of the three initial triplet populations become fitting parameters. Other adjustable parameters are the line width LW, the spin–spin coupling J, and the encounter rate k_{en}. The g factors and hyperfine coupling constants were taken from the literature values for the corresponding monoradicals.[10]

The simulations in Figure 1B are satisfactory with respect to both the overall shape and the time evolution of the EPR signal. The spectra are surprisingly sensitive to all five fitting parameters, and the very narrow range of error for LW, J, and k_{en} reported is an indication of the uniqueness of the fit. The value of k_{en} of 7.2×10^{10} s^{-1} is almost *2 orders of magnitude larger* than the free-solution value of 1×10^9 s^{-1}, and the J value is also larger than in solution (at this temperature in free solution, $J = -140 \pm 5$ MHz). Most likely the radical center closer to the surface has lost some of its rotational and translational degrees of freedom, removing access to conformations where the ends of the chain can best avoid each other. The line width is larger due to inefficient motional narrowing closer to the surface, a phenomenon also observed for monoradicals.[3]

An attempt to detect a spin-correlated radical pair whose members are anchored to two separate sites on the surface is shown in Figure 1B. Spin-polarized spectra are observed; however, they are extremely broad with no resolved hyperfine lines. The lack of features is indicative of multiple site occupancy, which stems from a lack of control of the attachment point in the synthesis of the precursor. The analogy in solution would be an EPR spectrum produced by a group of biradicals of many different chain lengths and therefore many different J couplings. However, it is interesting to note that the spin-polarization patterns evolves from predominantly absorptive to emissive/absorptive over just 300 ns, indicating that a fast k_{en} may also be present in this system.

The use of reactive biradicals as probes of diffusion phenomena in interfacial systems looks very promising with this powerful and informative experiment, and a detailed study of the effects of biradical chain length, solvent, temperature, surface morphology, and chemical composition is presently underway in our laboratories.

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Accurate Measurements of Proton Scalar Coupling Constants Using Carbon-13 Isotropic Mixing Spectroscopy[†]

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Vicinal coupling constants provide information about molecular conformations in solution which is complementary to nuclear Overhauser effect data.[1] Particularly important are $^3J(H^\alpha–H^\beta)$ coupling constants which are used to determine stereospecific $C^\beta H_2$ assignments[2] and to characterize side-chain conformations.[2,3] In large peptides and small proteins, however, broad resonance line widths result in heavily overlapped cross-peak components and complicate measurements of the associated coupling constants.[4] One approach for overcoming this problem is two-dimensional (2D) homonuclear exclusive COSY (E.COSY).[5-7] These methods use linear combinations of multiple-quantum filtered COSY experiments,[5] mixing pulses with small (≪90°) flip angles,[6] or frequency-selective shaped pulses[7] to restrict magnetization transfer

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