J. Am. Chem. Soc. 1989, 111, 2001-2003

lations are summarized and the thermochemistry involved is discussed.

In order to calculate the kinetic energy distributions, structures and vibrational frequencies for the various species are required. These were taken from the literature where possible, or estimated from literature values of similar species.[45] The details of the kinetic energy distributions were found to vary only weakly with structure or vibrational frequencies over the entire physically reasonable range for these quantities. The distributions were strongly dependent on the total energy available to the dissociating complex, and hence in our model to the ΔH° of reaction. Often all heats of formation of products and reactants were well known except one, the organometallic product ion. The heats of formation for Co(propene)$^+$, Co(carbonyl)$^+$, and Co(ethylene)$^+$ have been previously determined.[12b] The bond energies for the corresponding iron species have also been determined.[46] The heats of formation for cobalta- and ferracyclobutane were determined in this study and are consistent with the heats of formation inferred from ligand displacement reactions.[38] These heats of formation were consistently used throughout the calculations and are summarized along with the other parameters in Table VI–VIII.

Registry No. Fe$^+$, 14067-02-8; Co$^+$, 16610-75-6; $\overline{CH_2CH_2CH_2C}(O)$, 1191-95-3; $CH_2{=}CHCH_2CH_2CH_3$, 109-67-1.

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(45) (a) Shimanouchi, T. *Table of Molecular Vibrational Frequencies*, Consolidated, Vol. I; National Bureau of Standards: Washington, DC, 1972. (b) Sverdlov, L. M.; Kovner, M. A.; Krainov, E. P. *Vibrational Spectra of Polyatomic Molecules*; Wiley: New York, 1970.

(46) Heats of formation for Fe(propene)$^+$, Fe(carbonyl)$^+$, Fe(ethylene)$^+$, and for the ferracyclobutane ion were obtained by fitting the theoretical kinetic energy release distributions to the experimental distributions in all cases. A distinctive high-energy tail is observed for the experimental distributions which is not reproduced theoretically (see Figure 3b). In contrast, nearly exact fits were found for all the cobalt systems studied (see Figure 3a and ref 12b). The bond energies obtained by fitting the low-energy part of the distributions appears to be giving low bond energy values for iron relative to the corresponding cobalt species and relative to heats of formation inferred from ligand displacement reactions. As a result, the bond energies for the iron system are *rough estimates*. We are currently looking into the origin of these effects and will publish our results in a future publication.

Photophysical Recognition of Chiral Surfaces

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Abstract: We report that *R* and *S* quenchers [(*R*)-(+)- and (*S*)-(−)-*N*,*N*-dimethyl-1-phenethylamine, RQ and SQ] recognize differently an *R* excited-state chiral surface (silica derivatized with (*R*)-(−)-1,1-binaphthyl-2,2′-dihydrogen phosphate, RS). This is revealed by a ~30% difference in Stern-Volmer constants between RQ/RS and SQ/RS. A similar recognition difference was obtained between these quenchers and the corresponding *S*-(+) surface. The surface derivatization enhances the chiral recognition; in solution, no difference between the constants was observed. It is suggested that what we believe to be the first observation of a photophysical recognition of a chiral surface can be explained in terms of an increase in the relative weight of an exciplex formation (over ion-pair formation) quenching route and in terms of the decrease in the dimensionality of the quenching process.

Background

The crucial role of the geometry of the environment on reaction pathways in heterogeneous (photo)chemistry is now well established.[1] In surface photochemistry, the main relevant surface geometry parameters are the average pore size,[2] the degree of surface irregularity as determined through its fractal dimension,[3] and the geometry of the adsorbate–adsorbent interactions.[4] Here we wish to report that the *chirality* of a surface may affect the pathway of its photophysical interactions: in particular, that *R* and *S* quenchers recognize differently an excited state of an *R*-derivatized chiral surface, and that the same recognition difference exists between this pair of quenchers and an *S* chiral surface.

Chiral recognition in photoprocesses[5] carried out in chiral environments has been reported in several cases (e.g., crown ethers,[6a] dextrin,[6b] chiral crystals,[6c] enzyme[6d]), but we are unaware of any photochemical recognition of a chiral surface. Horner and Klaus[7] derivatized the surface of silica with a chiral photosensitizer but observed no effect on the cis–trans chiral photoisomerization of 1,2-diphenylcyclopropane. In spite of this specific unsuccessful case, the idea of a photophysical chiral surface recognition seemed to us feasible, not only in view of the observations in ref 6, but mainly because of the great progress and success in chromatographic separations of enantiomers.[8,9] These are clearly indicative of substantial differences in the interactions of two enantiomers with a chiral surface. For our purpose (see below) we notice, in particular, that the enantiomers of chiral amine compounds and of binaphthyl derivatives are separable chromatographically.[8,9] Consequently, from the various chiral photoprocesses reported for *homogeneous* solutions,[5] we chose to concentrate on the observation of Irie et al.[10] that the quenching of (unsubstituted)

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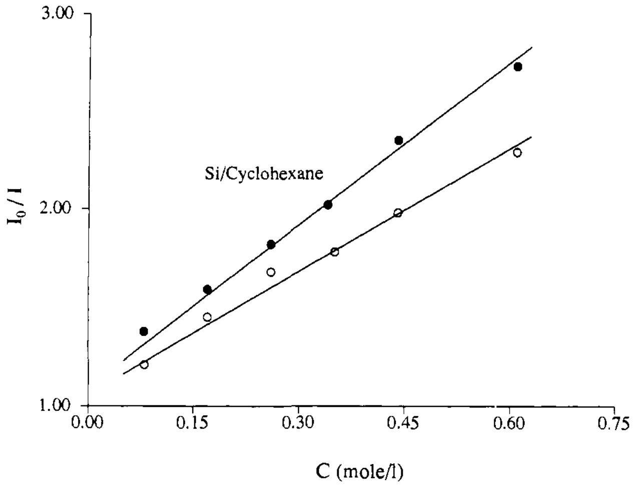
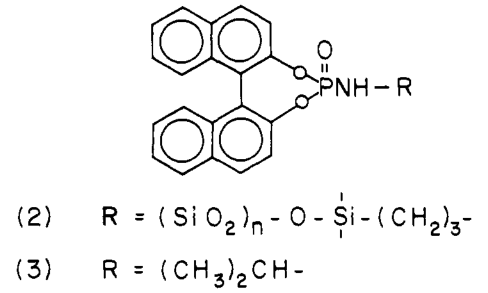


Figure 1. Fluorescence quenching of silica derivatized with (*R*)-(−)-1,1-binaphthyl-2,2-dihydrogen phosphate by (○) (*R*)-(+)- and (●) (*S*)-(−)- *N*,*N*-dimethyl-1-phenethylamine in cyclohexane slurry.

1,1-binaphthyl in solution is affected differently by the two enantiomers of *N*,*N*-dimethyl-1-phenethylamine (**1**, DPA). Thus, the chiral surfaces employed in this study are silica-60 surfaces derivatized with (*R*)-(−)- and (*S*)-(+)-1,1-binaphthyl-2,2-dihydrogen phosphate[11] (BNP), resulting in **2**. The excited state



(2) $R = (SiO_2)_n-O-\overset{|}{\underset{|}{Si}}-(CH_2)_3-$

(3) $R = (CH_3)_2CH-$

of **2** was then quenched by *R*-(+)-**1** and *S*-(−)-**1** in a solid/cyclohexane interface.

Experimental Details

Chemicals. The chiral compounds DPA and BNP were purchased from Sigma. The silica was Merck's Lichroprep 60.

Surface Derivatizations. Silica (7 g) was silylated with 14 mL of 3-aminopropyltriethoxysilane (Petrarch Chemicals) in dry toluene under reflux at 130 °C for 8 h. Unreacted surface silanols were then blocked by additional silylation with 5 mL of trimethylethylethoxysilane under reflux for an additional 8 h. The derivatized silica was then filtered and washed thoroughly with toluene, acetone, and methanol. BNP was then linked to the surface by phosphamidation of the amine[11] using DCC as a coupling agent in a chloroform slurry at room temperature for 4 h. The product **2** was then filtered and washed with chloroform, acetone, and methanol. Elemental analysis revealed full surface coverage. Compound **3** was synthesized similarly from BNP and isopropylamine (Sigma).

Fluorescence Measurements. **2** (70 mg) was diluted in a ratio of 1:10 with the propylamine–silica and slurried in 0.35 mL of cyclohexane or methanol. *R*- or *S*-**1** as added to this slurry, and the fluorescence intensities were measured with a Perkin-Elmer LS-5 spectrofluorimeter in a 1-mm cell in a front-face arrangement.

Results and Interpretations

The *R* surface revealed a 30% differences in the Stern–Volmer slopes with *R*-**1** and *S*-**1**. Characteristic Stern–Volmer quenching plots are shown in Figure 1; a ratio of 1.3 ± 0.1 between the Stern–Volmer slopes is observed (2.08 ± 0.10 and 2.76 ± 0.10 M^{-1} for *R*-**1** and *S*-**1**, respectively). A somewhat smaller ratio (but still in the same experimental range) of 1.2 ± 0.1 was obtained for the *S* surface (slopes of 2.24 ± 0.15 and 1.88 ± 0.15 m^{-1} for *R*-**1** and *S*-**1**).

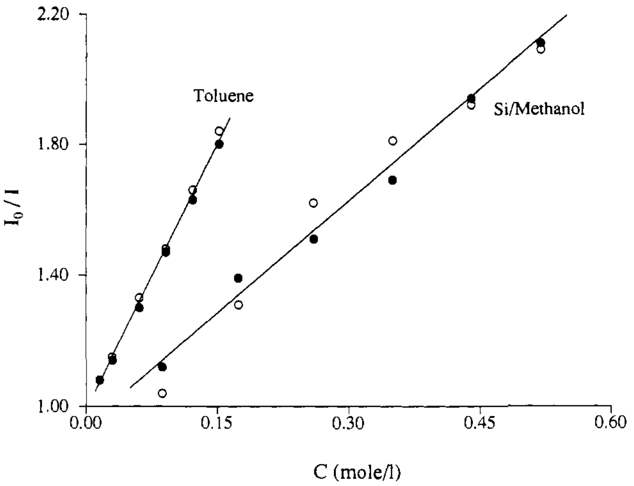
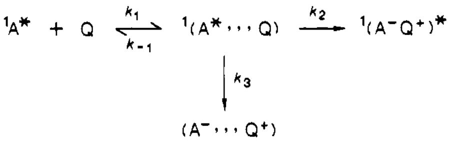


Figure 2. Same as Figure 1 in methanol slurry and molecule **3** in toluene solution.

Scheme I



Clues as to the underlying mechanism which allows the above chiral-surface discrimination come from three additional observations shown in Figure 2. First, when the interface was changed from surface/cyclohexane to surface/methanol, the chiral recognition disappeared (quenching slopes of 2.26 ± 0.10 and 2.16 ± 0.10 for *R*-**1** and *S*-**1**, respectively, with *R*-**2**); second, no chiral recognition was obtained with an analogous solution reaction, carried out between the excited state of the isopropylamide derivative **3** and the above quenchers (Figure 2); and, third, in the homogeneous toluene solution the quenching efficiences are more than twice as high as those of the derivatized surface; 5.53, 5.30, 5.41, and 5.27 ± 0.10 M^{-1} for the pairs *R*-**3**/*R*-**1**, *R*-**3**/*S*-**1**, *S*-**3**/*R*-**1**, and *S*-**3**/*S*-**1**, respectively.

The first observation can be rationalized, as already suggested by Irie et al.[10] for homogeneous solutions, in terms of a decrease in the relative weight of the exciplex-formation route, k_2, compared with the ion-pair route, k_3, between the acceptor (A, the derivatized surface) and the quencher (Q) according to Scheme I.[12] Formation of the exciplex $^1(A^-Q^+)^*$ requires specific close-range interactions between $^1A^*$ and Q which are sensitive to the mutual geometry of the reactants. Consequently, k_2 is strongly geometry dependent.[12,13] On the other hand, the ion-pair route (k_3) is associated with longer range electron transfer and is thus less sensitive to geometry. Since k_3/k_2 increases in polar solvents, chiral discrimination will decrease with increasing solvent polarity. This interpretation is indeed corroborated by the emission spectra shown in Figure 3a. In the cyclohexane/surface system, the quenching process is accompanied by the appearance of a red-shifted (λ_{max} 450 nm) emission, attributable to the exciplex,[12] which is absent when methanol is the interfacing solvent (Figure 3c). An alternative approach, attributing the observed chiral discrimination to effects associated with k_1 and k_{-1}, may also be suggested.[14] However, as in the case of homogeneous solutions,[10] it seems considerably less likely, principally since the donor-acceptor distance in the encounter complex, $^1(A^* \cdots Q)$, is assumed

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[14] We thank an anonymous referee for mentioning this possibility to us.

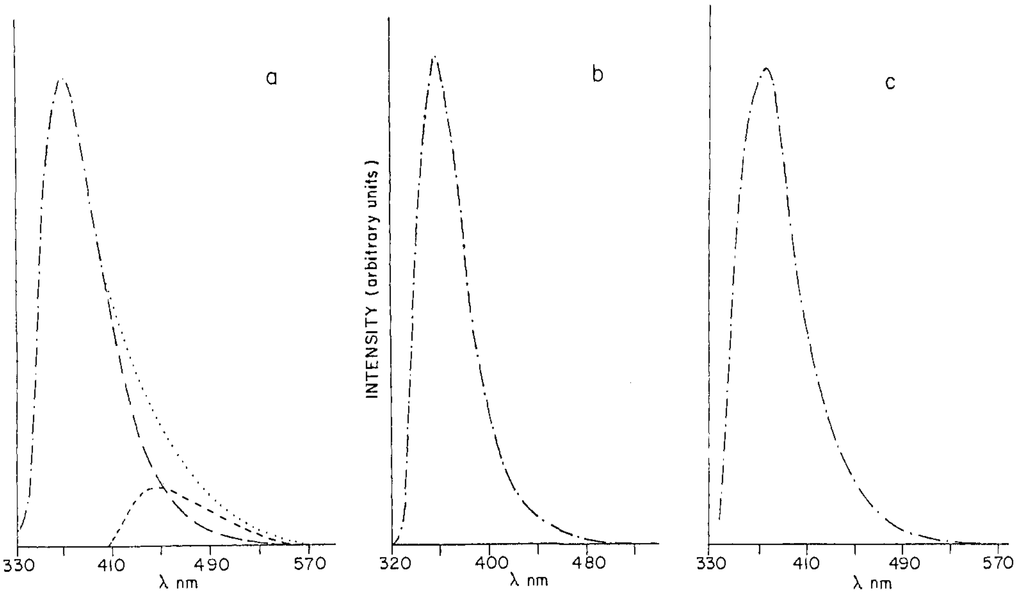

Figure 3. Emission spectra at $I_0/I = 3$ of (a) **2** in cyclohexane (--) without and (···) with **1** [(-·-·-) an overlap of these lines, (---) the calculated exciplex band], (b) **3** in toluene, and (c) **2** in methanol.

to be large (>5 Å; cf. ref 10b, p 5482), beyond that required for chiral recognition.

As mentioned above, the photophysical surface chirality effect should also be considered in view of the lack of chiral recognition of **1** + **3** in solution, which differs from the observation of Irie et al,[10] with the unsubstituted 1,1′-binaphthyl. Since the emission spectra of **1** + **3** in solution do not show the exciplex band (Figure 3b), the lack of chiral recognition in solution can again be attributed to a relatively inefficient exciplex route, i.e., to a $k_3 \gg k_2$ situation. A possible interpretation is to assume that the aryl moiety in **3** is sterically hindered by flip-flop movements of the isopropylamine side chain. We propose that this hindrance, which is absent in the unsubstituted binaphthyl, is also absent or at least less pronounced in the surface-bound chromophore, because of a combined effect of anchoring the side chain to the surface and exposing (one face of) the aryl moiety during a horizontally flat adsorption conformation of that moiety. This would be in keeping with the factor of 2 observed between the quenching rate constant of **3** in solution, as compared to that of **2** (BNP) on the surface (Figure 2); i.e., one side of the adsorbed molecule is shielded by the surface to quencher molecules approaching from the solution.

A second approach may again involve polarity considerations. As mentioned above, a highly polar solvent like methanol reduces drastically the k_2/k_3 ratio. However, it has been shown[12] that with some intramolecular arylamine exciplexes this trend may be reversed through a mechanism in which exciplex inhibition due to unfavorable arylamine geometries may be compensated by exciplex solvation forces, giving rise to an exciplex band. A comparable exciplex-solvating environment may be provided in the present system by neighboring, unreacted[11] propylamine groups.

One can also argue[14] that the observed differences between the Stern-Volmer plots of the two enantiomers reflect different (ground-state) chromatographic interactions between the amines **1** and the two enantiomers of the surface-bound **2**, i.e., that static, rather than the dynamic considerations mentioned above, prevail. However, for this type of quenching to be significant, a substantial fraction of the amine should be complexed to the ground-state binaphthyl, whereas for chromatographic separation of enantiomers, only a minimal degree of interaction with the surface is sufficient. In the absence of evidence for any such substantial ground-state complexation, we retain at present the excited-state approach as suggested in homogeneous solutions by Erie et al.[10] This approach is also supported by the observation (see above) that the quenching efficiency of the surface-bound aryl moiety **2** is smaller by only a factor of 2 with respect to the analogous process in homogeneous solutions. Such a factor, which may be attributed to a restricted accessibility of **2** on the surface to solution amine molecules, is in keeping with our dynamic quenching mechanism, i.e., with the assumption that the majority of the excited, surface-bound molecules are quenched via bombardment by amine molecules diffusing to the surface from the solution.

Finally, we draw attention to the possibility that adsorption enhances chirality because of the basic changes in molecular symmetry properties involved in that process. The problem, namely, what are the symmetry requirements of an object in two dimensions in order to show properties of left and right handedness, has been treated in detail both conceptually[15] and from the point of view of chiral heterogeneous catalysis.[16] The general result is that by reducing the number of degrees of freedom for interaction by hindering one side of the molecule (the side facing the surface), molecules which are achiral (in solution) become prochiral when adsorbed: namely, they become chiral with respect to an incoming (chiral) reagent. For instance, 1,2-substituted naphthalene is chiral in two dimensions while being achiral in solution. For our purposes this means that **1** is able in principle to recognize not only the three-dimensional chirality of the binaphthyl, but also the two-dimensional chirality of one of the 1,2-substituted naphthyl moieties. If the adsorption conformation is such that only one of the naphthyl moieties lies flat on the surface, an incoming reagnet (**1**) may use this moiety as additional information for chirality recognition.

Acknowledgment. Supported by the U.S.-Israel Binational Foundation (BSF) and by the Berman Foundation.

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