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Electron Transfer Photofragmentation Reactions in Monolayer Films at the Air/Water Interface

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A series of photoinduced electron-transfer fragmentation reactions have been studied in compressed monolayer films at the air/water interface. The reactions investigated involve amphiphilic and polymeric derivatives of fragmentable amino alcohol, 1,2-diamine, and pinacol donors and light-absorbing acceptors, which are reactive in solution-phase studies from their triplet states. For intralayer studies a surfactant anthraquinone derivative was the light-absorbing acceptor. For comparable "interfacial" studies, the water soluble cation tris(2,2′-bipyridine)ruthenium(II)$^{2+}$ (Ru(bpy)$_3{}^{2+}$) was the photoactive acceptor from the subphase. The fragmentation reactions all involve oxidative cleavage of a relatively strong C−C bond in the donor. Reaction was followed in each case by monitoring changes in surface pressure that occur when the compressed film is irradiated and maintained at a constant area. Reaction was readily observed in most cases where the donor and light-absorbing substrate are present; however the consequences were found to be quite dependent upon the specific donor substrate. Thus for simple single-chain amphiphiles containing either amino alcohol or 1,2-diamine donor sites, both intralayer and interfacial reactions result in rapid decrease in surface pressure, consistent with destruction of the film as the more hydrophilic redox products are solubilized into the subphase. For a polymeric diamine, much more complex behavior is observed, consistent with a situation where single fragmentation events do not lead to removal of material from the film but multiple fragmentation reactions culminate in film solubilization. Finally, a double-chain amphiphilic pinacol was found to undergo interfacial fragmentation with Ru(bpy)$_3{}^{2+}$ in the subphase with a concurrent increase in surface pressure to form stable films that do not "dissolve" into the subphase. The isotherms observed following irradiation, decompression, and recompression are consistent with an expansion that occurs as the two-chain amphiphile undergoes redox fragmentation to produce two equivalents of a single-chain amphiphile.

Introduction

Photoinduced single electron transfer (SET) reactions have been the focus of much experimental and theoretical investigation during the past 2 decades.[1] Although excited-state quenching by SET to produce highly reactive ion-radicals occurs efficiently in many different environments ranging from solution to polymers, within strands of nucleic acids, in peptides, and in other biopolymers, efficient net chemical reaction is only occasionally observed, due to the usually rapid return electron transfer processes that occur efficiently, especially when the quenching involves excited singlet states.[2] When triplet excited states undergo SET quenching, the probability of net photochemical transformations increases due to the spin retardation (by a factor of ~10^{-3}) of the return electron-transfer process.[3] Among the many possible reactions that can occur following SET redox are fragmentations of either the oxidized donor or reduced

acceptor, or both.[4] These reactions can be rather rapid and moderately efficient and they typically result in formation of a stable (even electron) product and a redox-active radical. In many cases the resulting radical is rapidly consumed in a subsequent dark redox event culminating in net two-electron oxidation or reduction of the substrate.

We and others have previously reported moderately efficient fragmentation reactions of donors, such as amino alcohols,[5] 1,2-diamines,[6,7] and electron-rich pinacols[8,9] by irradiation of light-absorbing acceptors in solution, and in polymers,[10] both in solution and in solid films. Corresponding reactions of fragmentable acceptors have also been observed for a variety of compounds including halides,[8] esters,[4a] and electron-deficient pinacols.[9] We

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have also examined tethered acceptor-fragmentable donor systems and find that although intramolecular quenching of acceptor luminescence by the donor occurs efficiently, efficient reaction only occurs when the acceptor excited state is a triplet.[3a] In the tethered systems as well as in the polymers, the holding of the donor and acceptor in close proximity and the elimination of diffusional processes increase the efficiency of both quenching and return electron transfer reactions. Nonetheless, the fact that net phototransformation occurs in both systems indicates that photoinduced SET reactions may not be restricted to fluid solutions and may be generally observable in organized media and other environments.

An intriguing medium for investigation of SET reactions is spread monolayer films at the air—water interface or supported Langmuir—Blodgett multilayer assemblies. The spread films offer a particularly attractive medium in that several different reaction possibilities exist. Thus, both electron donor and acceptor could be incorporated into the film or, alternatively, one of the reaction partners might be incorporated into the film while the other could be present in the subphase. Alternatives might include situations where both donor and acceptor are bound to the film by hydrophobic or electrostatic interactions. It is conceivable that the film environment could enhance, control, or restrict reactivity; at the same time it is reasonable to expect that reaction of a film component in one of the fragmentation processes discussed above could have major effects on the physical properties of the film. A number of studies extending back as far as 60 years ago have demonstrated both effects of the film environment (and properties such as degree of compression, etc.) on reactivity and the profound changes in film properties occurring as a consequence of reaction.[11−22] Although several examples of photochemical reactions in monolayer films have been studied, and a number of cases of photoinduced electron-transfer quenching in supported multilayers have been reported,[23−26] there have been relatively few investigations of photoinduced electron transfer resulting in net chemical change occurring in monolayer films.

In the present paper we report an investigation of SET photofragmentation reactions of amphiphilic and polymeric donors (amino alcohols, 1,2-diamines, and pinacols) in monolayer films at the air/water interface. We have investigated initiation of the reaction by irradiation of a light-absorbing acceptor (either anthraquinone or tris-(2,2′-bipyridine)ruthenium(II)$^{2+}$ (Ru(bpy)$_3$$^{2+}$)) reactive from a triplet state and present either as a cosurfactant in the film or as an ionic reagent from the subphase. We have observed chemically efficient reactions for several donor—acceptor pairs that can be readily followed by changes in the mechanical properties of the film (area/pressure, wettability, or solubility) and demonstrate the interesting and potentially useful consequences of these reactions in coatings or at interfaces.

Experimental Section

Materials. All chemicals were purchased from Aldrich and used as received unless specified otherwise. The syntheses of **4** has been described elsewhere.[10,27] **5** was synthesized by the same procedures used for simple alkylated aminopinacols.[8b]

Synthesis of 1. A classic Williamson ether synthesis scheme was used as follows: A 1.00 g (3.58 mmol) sample of 12-bromododecanoic acid in 5 mL of methanol was mixed with 0.502 g (8.95 mmol) of KOH. The combined mixture was refluxed for 4 h and later acidified with 10% aqueous HCl until it reached pH 5, assuming a cloudy appearance. The product was extracted into ethyl acetate, and removal of the solvent afforded 12-hydroxydodecanoic acid as a white powder (0.75 g, 97% yield) that was used without further purification. ^{1}H NMR (AcOD, 300 MHz): δ 3.25 (t, 2H, $J = 7.0$ Hz), 2.18 (t, 2H, $J = 7.0$ Hz), 1.89 (m, 2H), 1.72 (m, 2H), 1.27 (m, 14H).

Into 10 mL of dimethyl sulfoxide was suspended 0.750 g (3.46 mmol) of 12-hydroxydodecanoic acid, 1.15 g (3.81 mmol) of 2-(bromomethyl)anthraquinone, and 0.526 g (3.81 mmol) of K$_2$CO$_3$. After heating at 50 °C for 4 h, the reaction mixture was acidified with 10% aqueous HCl. The product was extracted into ethyl acetate, and the organic layer was washed four times with distilled water and once with brine. Removal of the solvent and recrystallization of the crude product from EtOAc/hexane afforded **1**, a light yellow powder (1.30 g, 89%). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 10.23 (s, 1H), 8.26 (m, 4H), 7.87 (m, 3H), 5.24 (s, 2H), 3.43 (t, 2H, $J = 7.0$, Hz), 2.38 (t, 2H, $J = 7.0$ Hz), 1.78 (m, 2H), 1.61 (m, 2H), 1.26 (m, 14H). The molecular weight was confirmed by mass spectrometry to be 438.5.

Synthesis of 2. To a solution of *trans*-stilbene oxide (2.0 g, 0.01 mol in 100 mL of anhydrous ethyl alcohol) was added *N*-methyloctadecylamine (2.85 g, 0.01 mol) in one portion at room temperature under N$_2$. The reaction was heated under reflux overnight and thin-layer chromatography (TLC) analysis showed the consumption of most of the starting materials. Ethyl alcohol was removed by rotary evaporation, and the residue was then chromatographed on silica gel with a 4/1 mixture of hexanes and ethyl acetate as eluent to produce 3.8 g (82%) of **2** as a colorless oil, which solidified upon standing at the room temperature. The compound was further purified by recrystallization from hot hexanes: mp 119−120 °C; ^{1}H NMR (CDCl$_3$): 7.19 (m, 6H), 7.03 (m, 4H), 5.37 (d, 1H), 3.50 (d, 1H), 2.39 (s, 3H), 1.46 (m, 2H), 1.22 (s, 32H), 0.92 (t, 3H). Anal. Calculated: C, 82.61; H, 11.13; N, 2.92; O, 3.33. Found: C, 82.90; H, 11.14; N, 2.89.

Synthesis of Diamine 3 (Scheme 1**).** 4-Octyl,4′-methyl-butanoate *trans*-stilbene (A) (1.02 g, 2.60 × 10^{-3} mol) was dissolved in 40 mL of freshly distilled dichloromethane in a 100 mL round-bottom flask (RBF) outfitted with a reflux condenser (protected with a drying tube) and N$_2$ inlet. 3-Chloroperbenzoic acid (620 mg, 3.60 × 10^{-3} mol) was added slowly. The reaction mixture was refluxed for 4 h and then stirred at room temperature overnight. The white solid was filtered and washed with methylene chloride. The organic solution was washed twice with 5% sodium bicarbonate solution. After drying over anhydrous Na$_2$SO$_4$ the methylene chloride solution was filtered; the solvent was removed by rotary evaporation. TLC (hexane/ethyl acetate 2:1 v/v) showed only one spot with $R_f = 0.77$. The solid was dried in a vacuum desiccator overnight affording 1.05 g (98%) of the *trans*-stilbene epoxide (B). Redistilled morpholine (10 mL, 0.115 mol) and *trans*-stilbene epoxide (600 mg, 14.70 × 10^{-3} mol) were combined in a two-neck 25 mL RBF equipped with a reflux condenser protected with a drying tube. The reaction was refluxed for 4 h under a slow positive nitrogen flow. TLC (hexane/ethyl acetate 2:1 v/v) showed no more starting material ($R_f$amino

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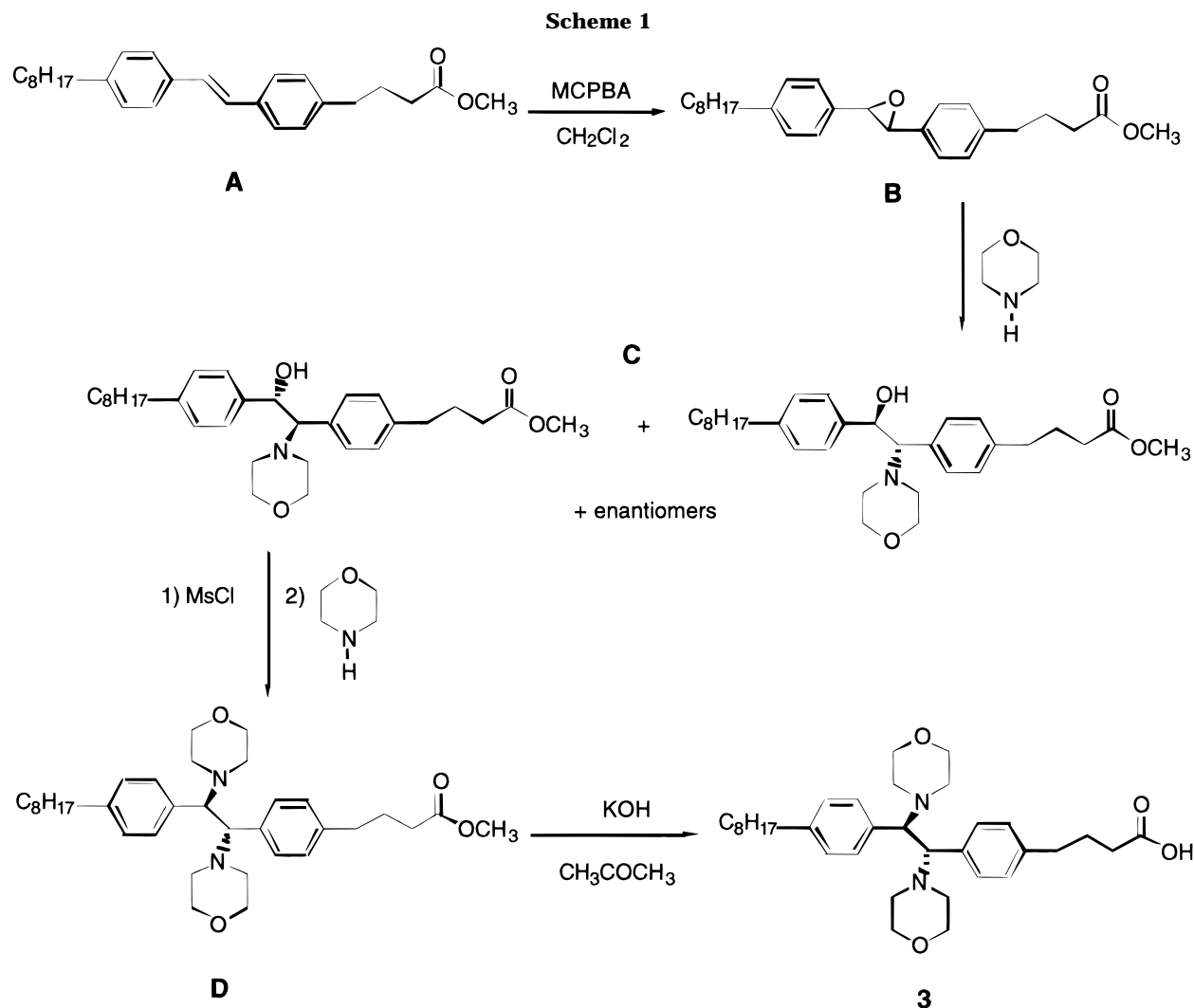(22) Balashev, K.; Panaiotov, I.; Proust, J. E. *Langmuir* **1997**, *13*, 5373.

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Scheme 1

alcohols = 0.20). A 60 mL portion of ethyl acetate was added to the flask, and the organic solution was washed three times with water, followed by saturated sodium chloride solution. After drying over anhydrous Na_2SO_4, the solvent was removed by rotary evaporation leaving 590 mg (81% yield) of a pale yellow oil (C). This mixture of enantiomers was used without further purification. The amino alcohol (C) (590 mg, 1.19×10^{-3} mol) was combined with 10 mL of freshly distilled methylene chloride and triethylamine (TEA) (150 μL, 1.19×10^{-3} mol) in a 25 mL three-neck RBF equipped with N_2 inlet, reflux condenser, and drying tube. The reaction solution was placed in an ice–salt bath until a temperature of −10 °C was reached, at which point methanesulfonyl chloride (MSCl) (160 μL, 1.55×10^{-3} mol) was slowly added via a syringe maintaining the temperature at −10 °C during the addition. The reaction was stirred at −5 °C for 30 min. TLC (hexane/ethyl acetate 2:1 v/v) showed just one spot at $R_f = 0.55$ indicating completion of the reaction. The ice–salt bath was removed, the methylene chloride was evaporated by a stream of nitrogen, and the crude product was dried in a vacuum desiccator for 1 h to remove unreacted TEA and MsCl. Morpholine (10 mL, 0.115 mol) was added at once and the reaction mixture was refluxed for 1 h. Methylene chloride (12 mL) was added, the organic phase was washed four times with water and saturated sodium chloride solution, and dried over anhydrous Na_2SO_4, and after filtration the solvent was removed by rotary evaporation. The crude product was passed through a silica gel column, using hexane/ethyl acetate 2:1 (v/v) as eluent. White solid erythro diamine ester (D) (500 mg, 74% yield) was obtained. Erythro diamine ester (382 mg, 6.77×10^{-4} mol) and four pellets of KOH were dissolved in 30 mL of acetone and 10 mL of water. The reaction mixture was refluxed for 1 h, then 12% HCl was added until the solution was acidic by pH paper. The acetone was removed by rotary evaporation, and the acid was extracted

with methylene chloride. The methylene chloride layers were joined and washed with water and saturated sodium chloride solution, and the solution was dried over anhydrous Na_2SO_4. After removal of the solvent, the crude product was purified by silica gel column chromatography using first chloroform and then chloroform/methanol (1:1, v/v) as eluents. The white, crystalline powder was dried overnight in a vacuum desiccator to give 225 mg (60% yield) of product **3**. ^1H NMR (400 MHz) in $CDCl_3$: δ 0.85−0.88 (t, 3H, CH_2-CH_3); 1.25−1.31 (m, 10H, $-CH_2-$); 1.59−1.63 (m, 2H, $-CH_2-CH_2-Ph$), 1.95−1.99 (m, 2H, $-CH_2-CH_2-Ph$); 2.22−2.26 (m, 4H, morpholine); 2.32−2.38 (m, 6H, CH_2-COOH, and morpholine); 2.57−2.61 (t, 2H, CH_2-Ph); 2.65−2.69 (t, 2H, CH_2-Ph); 3.23−3.27 (m, 4H, morpholine); 3.34−3.82 (m, 4H, morpholine); 4.03 (s, 2H, $-CHPhN$); 7.05−7.14 (m, 8H, Ph). Anal. Calcd for $C_{34}H_{50}N_2O_4$: C, 74.14; H, 9.15; N, 5.09; O, 11.62. Found: C, 73.91; H, 9.24; N, 4.79.

Preparation of Langmuir−Blodgett (LB) Monolayers. The water used for the subphase was deionized and purified using a Milli-Q UF Plus system equipped with a cotton filter (VWR) and a carbon filter (Millipore). The water was also passed through a reverse osmosis system (Millipore). The purified water was then stored in a 60 L plastic tank, and prior to use, the water was refiltered through a carbon filter, two ion exchange filters, and a UF cartridge. The final resistivity of the water was 18.2 MΩ cm with a pH of about 6. All work with $Ru(bpy)_3^{2+}$ in the subphase was done on a "baby" KSV 5000 LB trough having a length of 150 mm and a width of 332 mm (area = 2.49×10^4 mm^2). The trough was thoroughly cleaned prior to each experiment by a tap water rinse, a copious 95% ethanol rinse, followed by a chloroform (99.8%) rinse, and allowed to air-dry. Aqueous solutions of $Ru(bpy)_3^{2+}$ were made by dissolving 300 mg into 400 mL of Milli-Q water, which had a resulting concentration of 1.3 mM. The buffered basic subphase (pH =

10.0) used in this work was made by separately dissolving 5.3 g of Na_2CO_3 and 4.2 g of $NaHCO_3$ (to avoid forming an insoluble precipitate) into a total of 2 L of Milli-Q water.

All LB monolayers made on the $Ru(bpy)_3^{2+}$ subphase were prepared under minimal light conditions underneath a red plastic housing in order to avoid premature decomposition of the monolayers. All reagents were dissolved in 99.8% chloroform and made up as millimolar concentrations. The solutions that were not in use were stored at 5 °C to maintain stability. All solutions were used at room temperature and dispersed dropwise onto the aqueous subphase. Cosurfactant mixtures were made in situ, mixed well, and added immediately. Anywhere from 10 to 200 μL in volume was used in dispersing the surfactants onto the surface. The solvents were allowed to evaporate for several minutes in order to allow the surfactants to equilibrate on the surface.

Acquisition of Isotherms and Kinetics. A calibrated Wilhelmy plate attached to a pressure transducer was used to acquire the surface pressure as a function of compression. The maximum compression and pressure rates were 10 mm/min and 10 (mN/m)/min, respectively. Isotherms were obtained at 22 °C before and after each experiment to determine changes in surface area. For most of the work done, surface pressures did not exceed 20 mN/m, since several of the surfactant monolayers were unstable beyond this pressure limit and collapsed. Once the pressure was achieved, the barriers were allowed to slowly (at a rate <5 mm/min) migrate to their original position. Kinetic runs on the monolayers consisted of compressing the layer to a desired pressure (10 or 20 mN/m) and maintaining a constant area while monitoring the surface pressure area changes. Irradiation of the monolayers was done using a medium-pressure mercury penlight (5 cm, Oriel) that was held at a constant distance of 6 cm from the top of the subphase. Control experiments were done with inert surfactants such as arachidic acid whose kinetic plot showed negligible change upon exposure to the light. Most of the monolayers having a reactive donor (and either **1** on the surface or $Ru(bpy)_3^{2+}$ in the subphase) displayed a discernible change in surface pressure upon exposure to the irradiating source. Irradiations were usually conducted for no more than several minutes. Control irradiation experiments done without $Ru(bpy)_3^{2+}$ in the subphase in the presence of a monolayer of a reactive surfactant donor amine show no changes, confirming that $Ru(bpy)_3^{2+}$ is absolutely essential for a reaction to occur at the air/water interface.

Results and Discussion

In this study we have examined photoinduced electron-transfer reactions involving two different arrangements of donor and acceptor substrates. In one group of investigations we have used amphiphilic donor and acceptors both present in a film at the air–water interface ("intrafilm" reaction) while in the second we have placed the donor in a film at the air–water interface and the light-absorbing acceptor as a water-soluble cation in the aqueous subphase ("interfacial" reaction). The specific substrates and reactions chosen for investigation are based on the reactivity of similar reagents in well-characterized photoinduced electron-transfer fragmentations and their structures are shown in Chart 1. The anthraquinone-derivatized fatty acid **1** was selected as an acceptor, potentially reactive from its triplet state, and to be used as the light-absorbing reagent in all "intrafilm" reactions. In several previous studies we have found that structurally similar anthraquinones can initiate photoinduced fragmentation of diamine donors with quantum efficiencies near unity.[3a,10] The acceptor chosen for investigation of "interfacial" reactions was the very well-studied cation tris(2,2′-bipyridine)ruthenium(II)$^{2+}$ ($Ru(bpy)_3^{2+}$), which has been found to participate with moderate efficiencies in a number of photoinduced electron-transfer reactions, including fragmentation reactions. Both of these acceptors absorb the output from the medium-pressure mercury lamp used in these studies (intense lines at 313 and 366

nm): the anthraquinone acceptor absorbs only the 313 line with an extinction coefficient $\epsilon = 1.02 \times 10^3 \, M^{-1} \, cm^{-1}$ while the $Ru(bpy)_3^{2+}$ absorbs both wavelengths and has an extinction coefficient about 10 times that of the anthraquinone.

The four donors used in this study are all reasonable amphiphiles that form good films at the air–water interface, which show reasonable compression behavior; films of all four substrates may be transferred to form Langmuir–Blodgett multilayers on glass or quartz supports. For the amino alcohol (**2**) and donor pinacol (**5**) amphiphiles, the reactive substrate is at the "hydrophilic" end of the amphiphile and thus is expected to locate at the aqueous interface. In contrast, the amphiphilic diamine (**3**) has the diamine several carbons removed from the hydrophilic carboxyl terminal. The diamine polymer (**4**) is less well-defined as an amphiphile, but it might be anticipated that the moderately polar diamine functionalities are close to the aqueous interface. Chart 2 shows the *initial* photoinduced electron-transfer fragmentation products anticipated from the four donors used in the study and the products that may be anticipated upon subsequent redox and hydrolysis reactions of reactive intermediates.[28]

Films at the air–water interface containing only **1**, **1** with arachidic acid, donor substrates **2**–**5**, either pure or in mixtures with arachidic acid, were all found to be stable upon irradiation with the medium-pressure mercury source. Little or no changes in the films as indicated by monitoring with the film balance during irradiation or by comparing compression behavior prior to and after irradiation were observed. In contrast, major changes can be observed by either monitoring technique when films containing both one of the donors and **1** are irradiated. Similarly, films of the donors (with or without arachidic acid) irradiated over a subphase containing $Ru(bpy)_3^{2+}$ showed major changes easily followed by maintaining the film balance at a constant area and monitoring pressure changes or by comparing isotherms measured before and after irradiation. Since the changes observed were quite dependent upon the substrate and acceptor combination as well as the presence of additives to the film or subphase, it is instructive to discuss each substrate's behavior individually and then comparatively evaluate the overall results.

Amino Alcohol (2). Films at the air–water interface containing only anthraquinone **1** and amino alcohol **2** are stable in the dark, provided the ratio of **2:1** is greater than 1.0. At a 1:1 ratio or lower, the anthraquinone evidently slowly dissolves in the subphase. Irradiation of films held at constant area after compression to a pressure of 10 mN/m with a medium-pressure mercury lamp results in a fairly rapid decrease of pressure, consistent with removal of material from the film (Figure 1). With ratios of **2:1** of 2:1 or less, the drop in pressure within 1.0 min of irradiation ($t_{1/2} \sim 0.5$ min) reaches ca. 0–1 mN/m, indicating nearly complete removal of the film from the surface. It is fairly clear from these experiments that both products of the photoreaction are rendered water soluble and removed from the film. The fact that a moderate excess (4:1) of the amino alcohol can be removed from the film upon irradiation suggests that the anthraquinone may be recycled, presumably by air oxidation of the semiquinone radical (or other intermediates)

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(28) Since only ca. 10^{14} molecules react in a given film at the air/water interface and in many cases the product "escapes" into the subphase, it is not feasible to carry out either qualitative or quantitative analysis of the products formed from the films. In each donor–acceptor case studied, the products produced from reaction in homogeneous solution were verified to be those indicated in Chart 2.
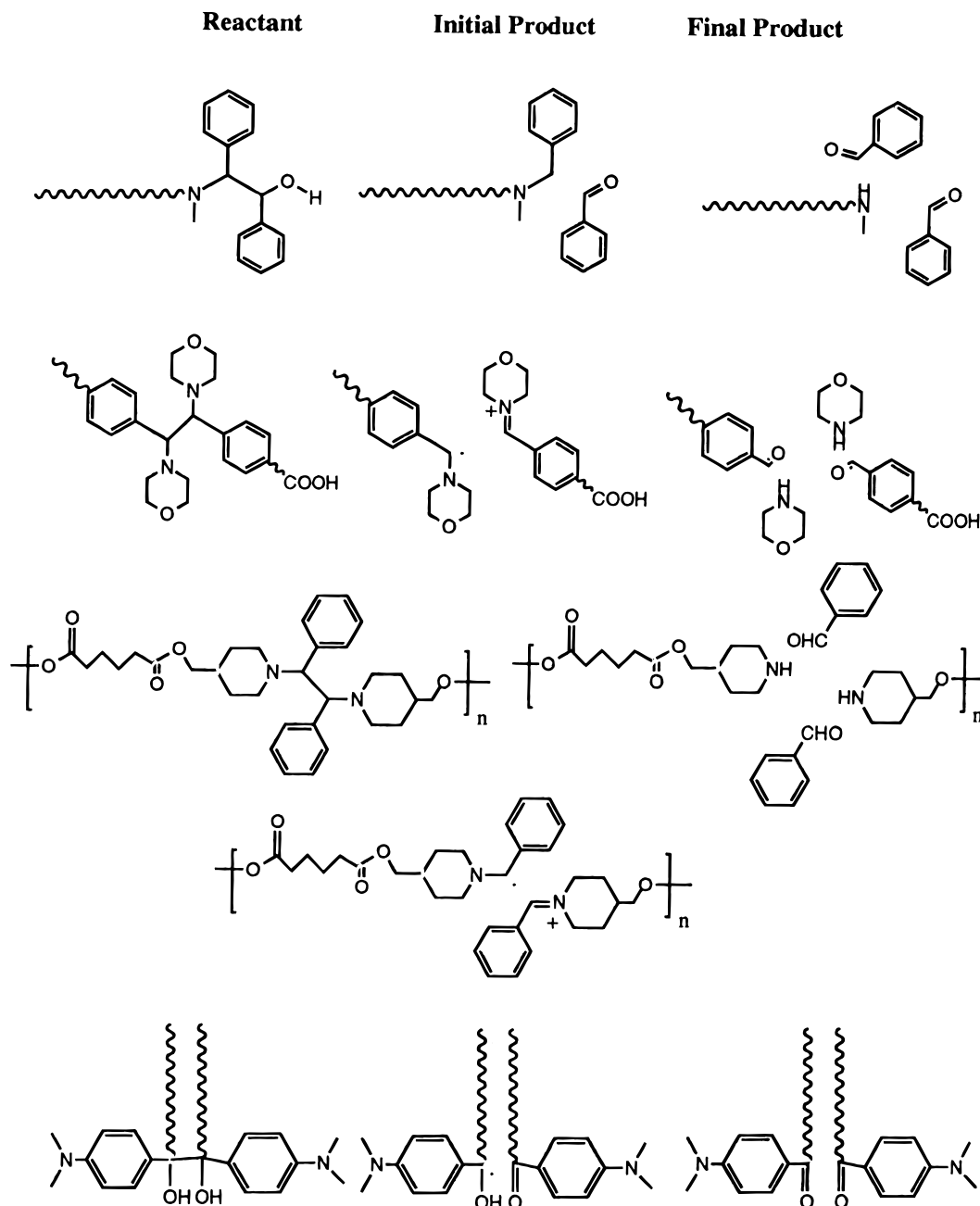
Chart 1.   Structure of Electron Donors and Acceptors
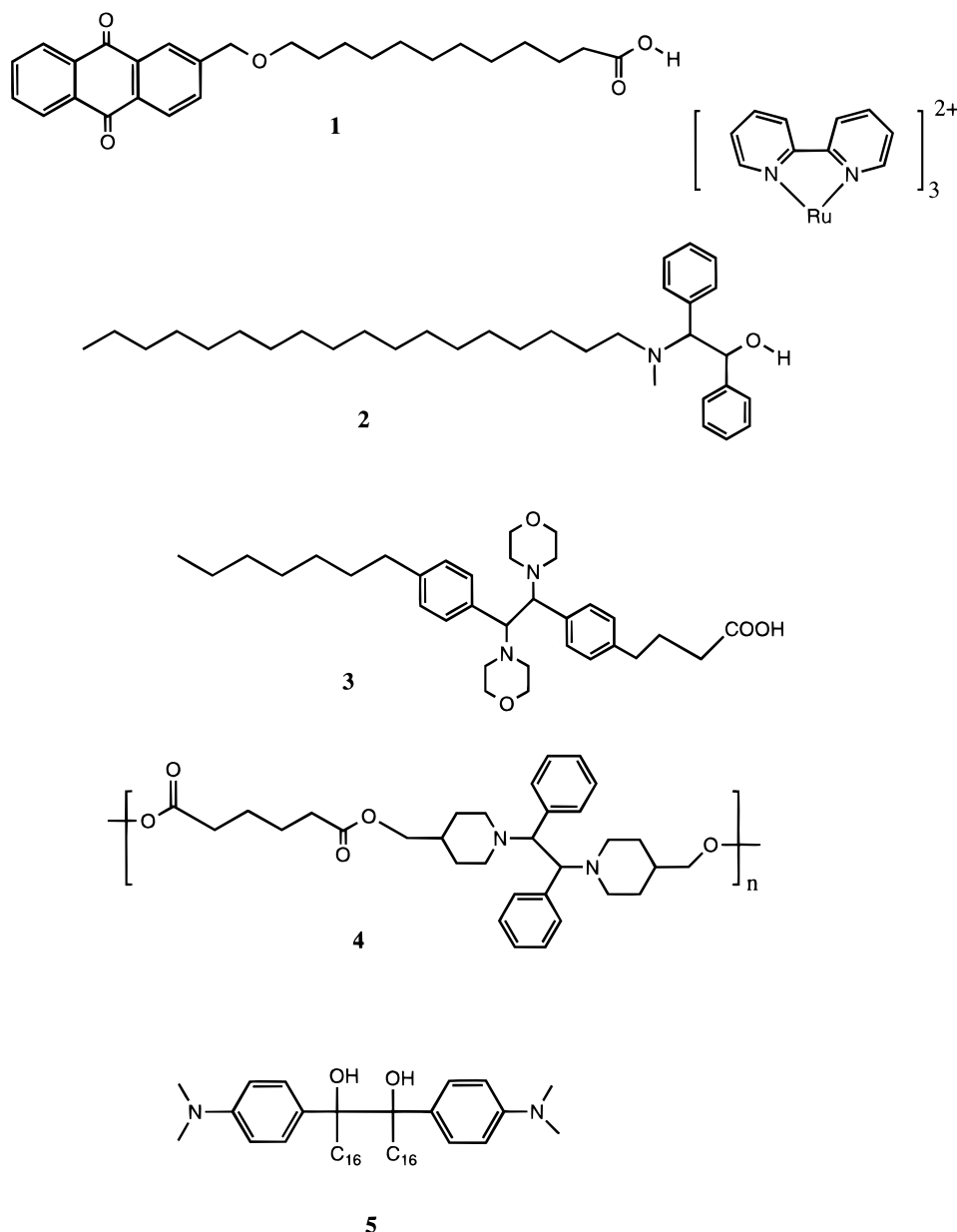
generated in the photoredox reaction. When the film is compressed to 20 mN/m prior to irradiation, the reaction is observed to proceed similarly with again a drop in film pressure to near 0 mN/m upon irradiation for several minutes; however the $t_{1/2}$ in this case is somewhat longer (~1 min) suggesting that compression somewhat attenuates the overall process. Addition of arachidic acid (AA) as a component of the film-forming mixture leads to a marked attenuation of the photoreaction as followed by decrease in pressure on irradiation of films at constant area as shown in Figure 2. From the leveling-off that is observed, it seems clear that arachidic acid not only attenuates the overall photoredox reaction but also remains in the film following completion of the reaction. That arachidic acid attenuates the reaction is shown most clearly by comparing the **2/1** (1:1 ratio) film with a film containing **2/1**/AA in a 1:1:1 ratio (Figures 1 and 2); for the former there is almost complete disappearance of the film upon irradiation while for the latter almost no reaction is observed. The attenuation is rather remarkable, but relatively easily understood. For **1** the acceptor chromophore is at the hydrophobic end of the amphiphile, and

in a well-organized film it should be at least 16 Å away from the amino alcohol donor of **2**. Thus quenching should be relatively inefficient, even when donor and acceptor are nearest neighbors, if the films are well-mixed. Addition of AA increases the separation and may even better organize the film. Thus it appears likely that whenever the mole percent of AA approaches 40 or 50%, there is insignificant quenching of the triplet of **1** by **2** and hence very little reaction. The isotherms obtained for mixtures of **1**, **2**, and AA suggest that a reasonable degree of mixing occurs.

For the interfacial studies, films of either pure **2** or mixtures of **2** with AA were irradiated over a subphase containing millimoles per liter $Ru(bpy)_3^{2+}$. Figure 3 shows the very rapid drop in surface pressure (area constant) upon irradiating a film compressed prior to irradiation to a pressure of 20 mN/m. The reaction has a $t_{1/2} \sim 20$ s, which is somewhat faster than for the reaction initiated by irradiation of **1** in the intralayer studies. That reaction occurs at all in pure films of **2** over a subphase containing $Ru(bpy)_3^{2+}$ is at first surprising since it might not be anticipated that the ruthenium cation would associate

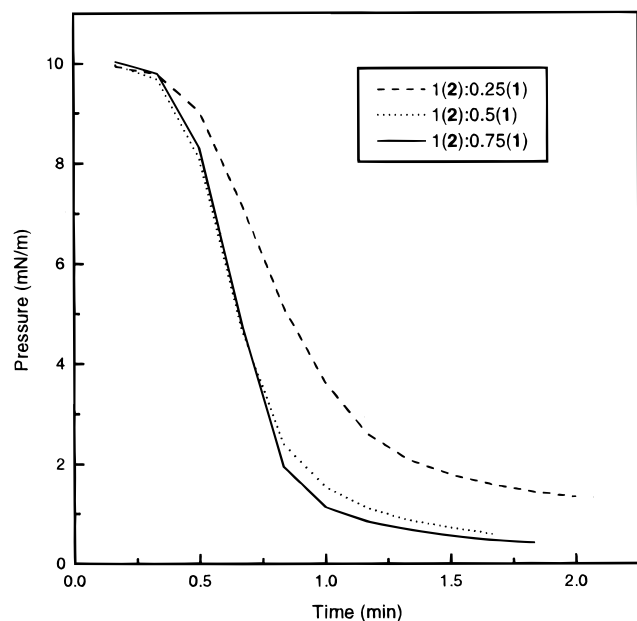**Chart 2. Donor Reactants, Intermediates, and Final Products**

Reactant	Initial Product	Final Product

strongly with a neutral film. However, since relatively little, if any, reaction would be anticipated by activation of Ru(bpy)$_3{}^{2+}$ in the "bulk" subphase, it must be inferred that there is some association, probably by a "hydrophobic" interaction between the organic cation and the film. Interestingly, adding AA to **2** over a neutral (pH = 6.6–6.8) subphase containing Ru(bipy)$_3{}^{2+}$ results surprisingly in a less rapid reaction. While the presence of AA should provide an anionic interface assisting binding of the ruthenium cation to the film, irradiation of a film formed from a 1:1 molar ratio of **2** and AA leads to a reaction about 50% slower than that for films of **2** alone. It is not possible to determine precisely the reason for the decrease in reactivity when AA is included in films of **2**, but several possible factors may be identified. First, if it assumed that aromatic–aromatic interactions between molecules of **2** favor some aggregation or "demixing"[29] the films may consist of "zones" of **2** and AA, which may actually tend

to sequester the Ru(bpy)$_3{}^{2+}$ away from the regions rich in **2**; however the isotherms suggest that the films are fairly well mixed. Another possibility is that a limiting factor in the fragmentation of **2**$^{\bullet+}$ following its formation by SET quenching is base-assisted deprotonation of the ion-radical. We and others have previously shown that the oxidative fragmentation of amino alcohols can be acceler-ated substantially by assistance of either the acceptor ion-radical or other bases added to the medium.[5a,30] In fact the relatively rapid reaction in the films of pure **2** in the presence of Ru(bpy)$_3{}^{2+}$ might be attributed in part to an enhanced activity of OH$^-$ at the film–water interface due to the concentration of the ruthenium cations. Examina-tion of the compression isotherms of unirradiated and irradiated mixed films of **2** with AA indicates that selective

(29) Furman, I.; Geiger, H. C.; Whitten, D. G.; Penner, T. L.; Ulman, A.; Langmuir **1994**, *10*, 837.

(30) Lucia, L. A.; Burton, R. D.; Schanze, K. S. *J. Phys. Chem.* **1993**, *97*, 9078.

Figure 1. Observed surface pressure changes upon irradiation of films of amino alcohol (**2**)−anthraquinone (**1**) over neutral subphase following an initial compression to 10 mN/m.
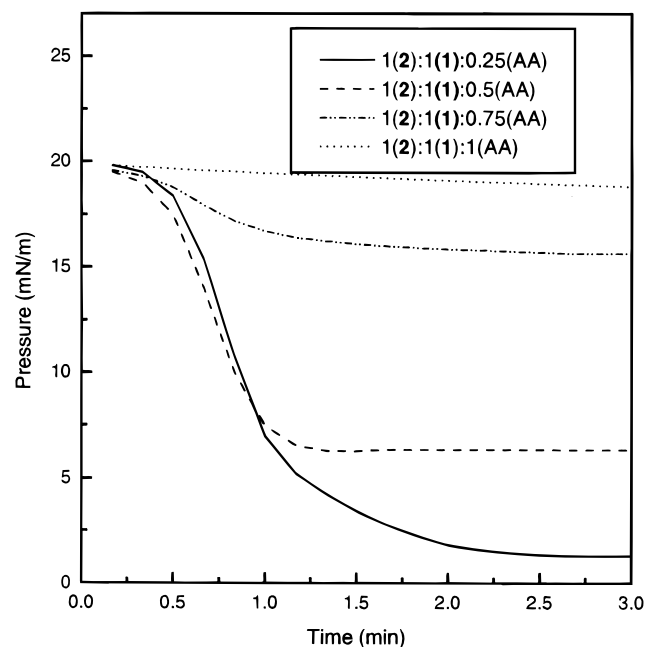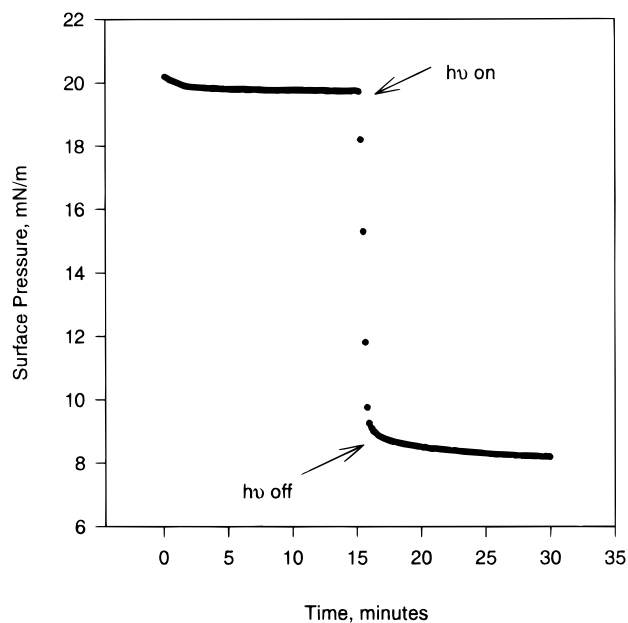

Figure 3. Change in surface pressure observed upon 20 s irradiation of a film of **2** formed over neutral subphase containing $Ru(bpy)_3^{2+}$ with an initial film compression to 20 mN/m.
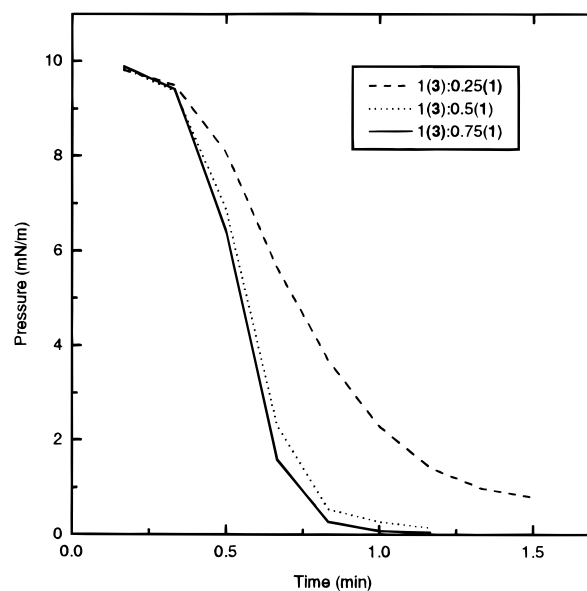

Figure 2. Kinetics (surface pressure changes) for irradiation of films formed from a 1:1 mole mixture of **1** and **2** with various concentrations of arachidic acid (AA). Neutral subphase with initial compression to 10 mN/m.

Figure 4. Kinetics (surface pressure changes) for irradiation of films of diamine **3**−anthraquinone **1** over neutral subphase following an initial compression to 10 mN/m.

removal of **2** occurs upon irradiation; however, unlike the mixed films of **1**/**2**/AA examined in the intralayer studies, addition of AA to the interfacial system **2**/$Ru(bpy)_3^{2+}$ does not result in elimination of reaction. Changing the subphase pH from 6.6 to 10 was found to produce relatively little change in the reaction profile.

Diamine 3. The diamine **3** is a very well-behaved surfactant in films at the air−water interface, either pure or in mixtures with AA or **1**. Irradiation of the anthraquinone and diamine in organic solutions with a medium-pressure mercury lamp leads readily to the detection of the two aldehydes and morpholine formed by the fragmentation and subsequent hydrolysis of the intermediate iminium cations. (Chart 2) Intralayer

studies of **3** with **1** in films either with only the donor and acceptor or with AA included led to results qualitatively and quantitatively similar to those obtained in the intralayer studies of amino alcohol **2** with **1**. Even with a 3-fold excess of **3** over **1**, there is a decrease in pressure to near 0 mN/m suggesting complete reaction and subsequent removal of both donor and acceptor into the subphase. Figure 4 shows the change of pressure occurring on irradiation for different mixtures of **1** and **3**, compressed to a initial pressure of 10 mN/m. As was observed for amino alcohol **2**, increasing the initial pressure to 20 mN/m results in a slightly slower reaction, as monitored by the change in pressure upon irradiation. Interestingly, when AA is added to films of **3** and **1** there is once again attenuation of the reaction (Figure 5), but the net attenuation observed is significantly lower in the case of the diamine compared to that with the amino
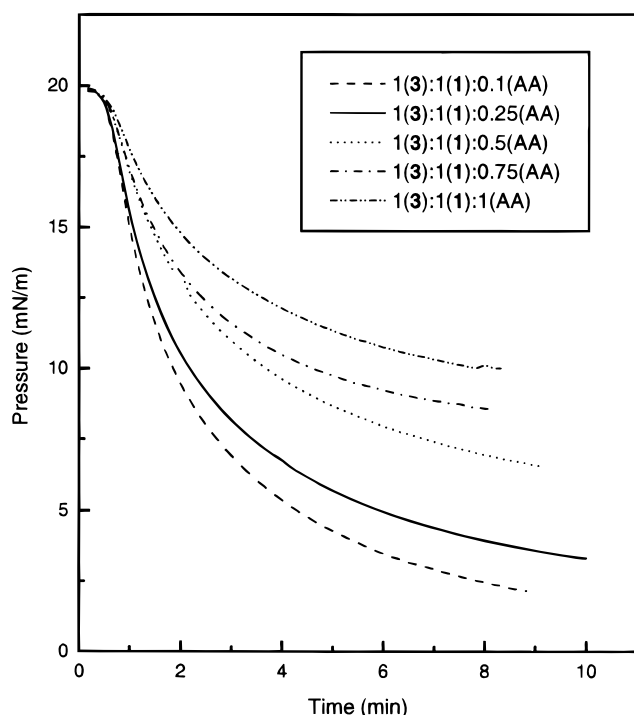
Figure 5. Kinetics (surface pressure changes) for irradiation of films formed from a 1:1 mole mixture of **1** and **3** with various concentrations of AA. Neutral subphase with initial compression to 20 mN/m.

alcohol. The isotherms of mixtures of **1**, **3**, and AA suggest that these films may be less well-mixed than those with **2**, and this might account for part of the differences. However a second possibility is that the edge—edge distance between donor and acceptor is considerably less in the case of **1** and **3** than between **1** and **2** such that the initial electron-transfer quenching may be much more attenuated in the latter case.

In the interfacial studies with **3** in films at the air—water interface and Ru(bpy)$_3^{2+}$ in the subphase, once again results qualitatively similar to those obtained with amino alcohol **2** are observed; however here the reaction appears to be slower by about a factor of 10 when monitored by decrease in the surface pressure of the film. When AA is added to the films, only a slight decrease in reactivity is observed and the difference for films of **3**/AA compared to films of **2**/AA is only about a factor of 2.

The apparent differences in reactivity between diamine **3** and amino alcohol **2** in the interfacial reactions are at first surprising, in view of the increased reactivity of similar nonsurfactant diamines compared with amino alcohols in solution. Typically the fragmentation rate constant for the diamine cation-radical is larger by as much as a factor of 100 than that for the amino alcohol cation-radical.[1e] However, two important factors need to be considered in attempting to compare reactivity in the films. First, the two donor reactants are at quite different sites, both with respect to the intralayer acceptor and the air—water interface. Considering the latter first, the location of the amino alcohol functionality in direct contact with the interface provides a situation where the "intermediate" products (Chart 2) are subject to rapid hydrolysis and should easily "escape" into the subphase following hydrolysis.[14-17] Also, as pointed out above, the location of the amino alcohol at a hydrophilic site where base-assisted fragmentation may occur may also attenuate the differences in fragmentation reactivity between the amino alcohol and diamine. In contrast, the diamine **3** has the

donor imbedded several carbons (~5.4 Å) into the presumed hydrophobic portion of the film such that the intermediate generated may survive much longer before hydrolysis, followed by "escape" into the subphase, can occur. In fact, earlier studies of lactone hydrolysis[15,16] and olefin oxidation[14] have suggested that compression-induced changes in the location of a functionality can strongly affect rates of reaction with subphase components. While this alone may account for the observed differences, there is also the possibility that the different distances between donor and acceptor may play a role. In the interfacial reaction, the amino alcohol's presence at the air—water interface may facilitate reaction compared to the diamine, especially in the neat films. The attenuation of the apparent difference in reactivity as AA is added could be attributed to a persistence of binding of the ruthenium cation to the diamine carboxyls while selective binding to AA in the films of **2**/AA may slow reaction in the latter situation by increasing the donor—acceptor separation. In the intralayer reactions the probable separation of donor and acceptor is considerably greater for the amino alcohol than for the diamine. While the small difference in reactivity in films containing only donor and acceptor might be attributable to more facile hydrolysis and escape of the products from the amino alcohol, the lower attenuation of the reaction for the diamine upon addition of AA is probably consistent with a lower attenuation of the quenching due to the smaller donor—acceptor separation in the films of **1**/**3**/AA.

Diamine Polymer 4. The polymeric 1,2-diamine **4** was found to form reasonable films (as assessed by compression isotherms) when spread from chloroform at the air—water interface. These films, either pure or containing simple amphiphiles such as **1** or AA, could be transferred by normal dipping techniques to form Langmuir—Blodgett multilayers. The LB multilayers of **4** containing **1** pulled from the water surface were found to be hydrophobic and only poorly wettable. Following irradiation with the mercury lamp, the areas exposed to light were found to be relatively hydrophilic and easily wettable.

Films of **1** and **4** at the air/water interface were found to show very different behavior under irradiation compared to those of the simple diamine and amino alcohol substrates previously described. As shown in Figure 6, a film of **1** and **4** in a 1:1 mole ratio (based on diamine and anthraquinone units) compressed to 10 mN/m undergoes an increase in pressure during irradiation, followed by a gradual decrease as the irradiation continues. The observed increase in pressure may be correlated with the swelling or "explosion" indicated for the irradiated LB multilayers in atomic force microscopy studies.[31] In contrast, irradiation of a similar film, compressed to 20 mN/m, results in a monotonic decrease in pressure, which may be attributed to loss of the photoproducts from **1** or **4** or both. Interfacial reaction between pure films of **4** and Ru(bpy)$_3^{2+}$ in the aqueous subphase was also investigated; Figure 7 shows the results of irradiation of films containing **4** with and without AA over ruthenium subphases. Here, as with the films of **2** and **3**, there is a drop in pressure accompanying irradiation, most consistent with removal of material as a consequence of the photolysis. The drop in pressure is not as great as that with the films of **2** and **3**, and it occurs much more slowly. The results from both the intralayer and interfacial photolyses are consistent with fragmentation between diamine groups in the polymer; the differences between

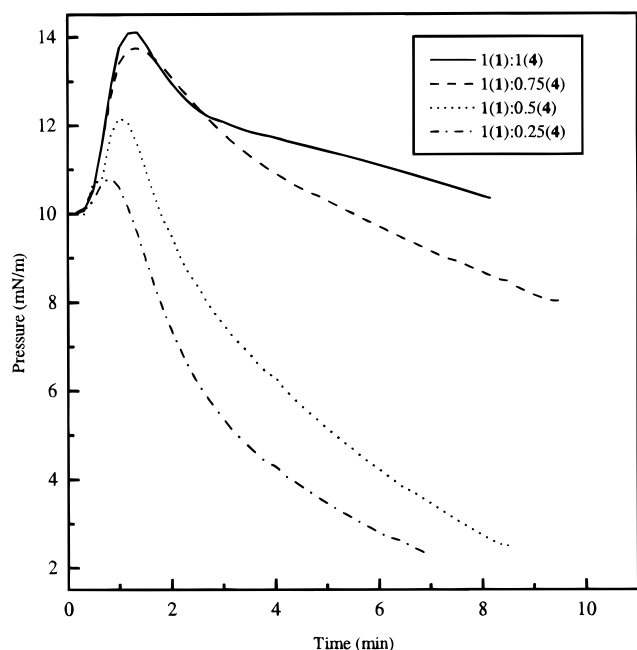(31) Wyrozebski, K. Unpublished results.

Figure 6. Kinetics for irradiation of films of mixtures of diamine donor polymer **4** with anthraquinone **1** formed over neutral subphase and compressed to an initial surface pressure of 10 mN/m.
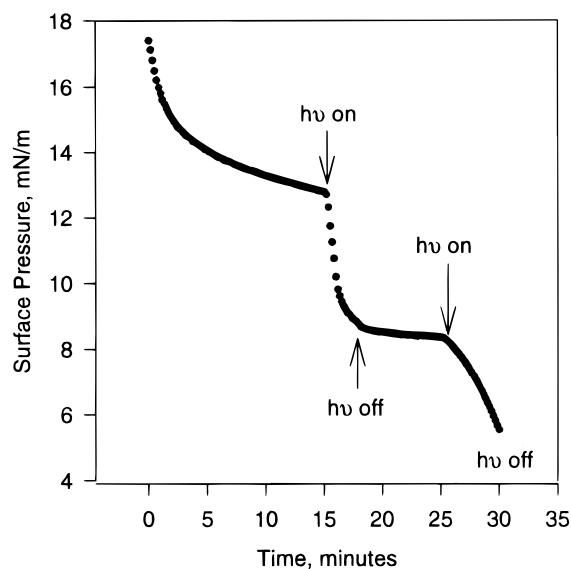

Figure 8. Isotherms for compression of donor polymer **4** over neutral subphase containing $Ru(bpy)_3^{2+}$: ●, first compression; ■, second compression following decompression; ▲, compression after 8 min of irradiation.

Figure 7. Change in surface pressure observed upon sequential 3 and 5 min irradiation of a film of donor polymer **4** formed over a neutral subphase containing $Ru(bpy)_3^{2+}$.

Figure 9. Change in surface pressure observed upon 1 min irradiation of films of pinacol **5**/AA mixtures over neutral subphase containing containing $Ru(bpy)_3^{2+}$.

reaction of the simple diamine and amino alcohol and that of **4** are readily attributable to the fact that a single cleavage event does not render the polymer sufficiently hydrophilic to solubilize it into the aqueous subphase. In fact the rise in surface pressure for the films of **1** and **4** compressed to 10 mN/m is consistent with a "swelling" of the polymer upon initial fragmentation, which may be reasonable, especially in consideration of the results observed with donor pinacol **5** (see below). As subsequent fragmentation events occur and the polymer is degraded to small hydrophilic fragments, the film is solubilized into the subphase. This is clearly shown by the isotherms obtained prior to and after irradiation (Figure 8).

Donor Pinacol 5. The donor pinacol undergoes a comparable electron-transfer fragmentation to that of amino alcohol **2** and diamine **3** upon reaction with
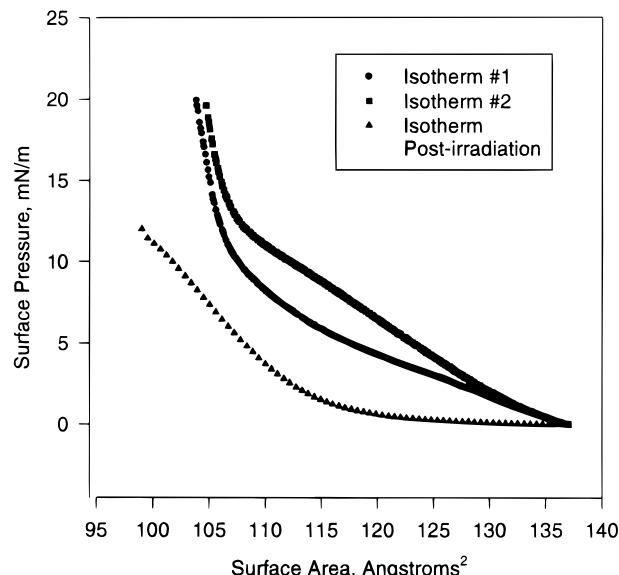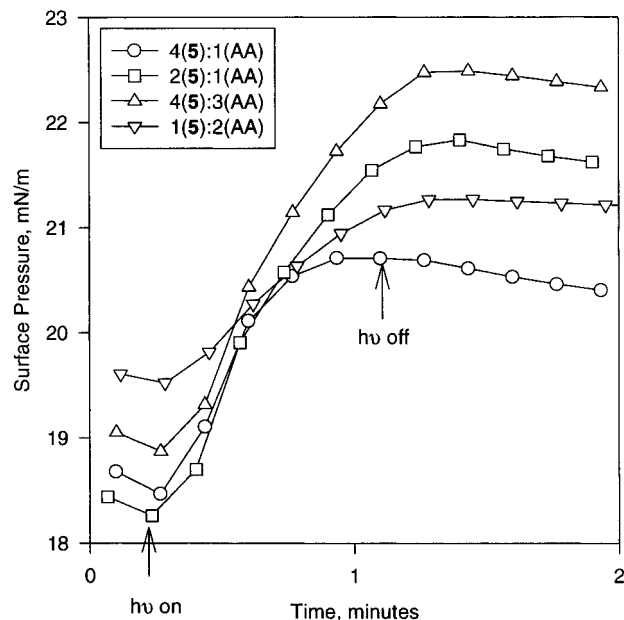
photoexcited acceptors, and the anticipated products are outlined in Chart 2. Although an intralayer study between **1** and **5** was not carried out, the reaction between films containing **5** and $Ru(bpy)_3^{2+}$ was examined with the observation of significant differences from the studies described above. For the interfacial studies with **5** in the films at the air−water interface and $Ru(bpy)_3^{2+}$ in the aqueous subphase, it was found that irradiation always leads to an **increase** in surface pressure as the area is maintained constant as illustrated in Figure 9. The films remain stable following the irradiation; as shown in Figure 9 the change in surface pressure for mixed films of AA and **5** ranges from ∼10 to 20% with the largest changes for the samples richest in **5**. Isotherms of films compressed prior and after irradiation also show an increase in area anticipated on the basis of the "kinetic" plots (Figure 10). The difference between the behavior of films of **5** and the
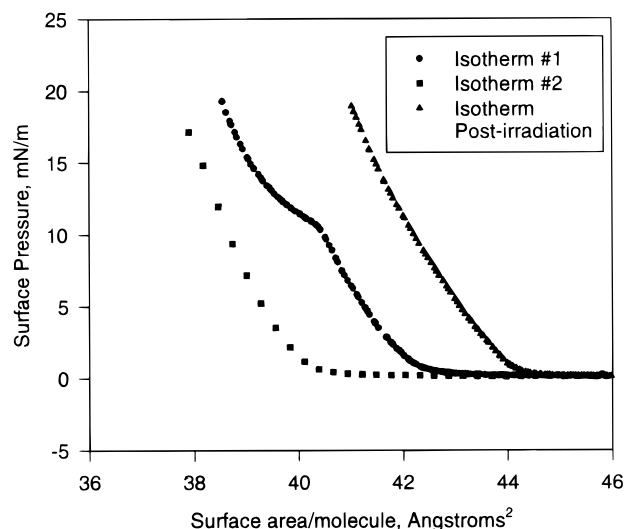
Figure 10. Isotherms for compression of pinacol **5** over neutral subphase containing Ru(bpy)$_3$$^{2+}$: ●, first compression; ■, second compression following decompression; ▲, compression after 7 min of irradiation.

corresponding diamine and amino alcohol is readily attributable to the specific cleavage of the pinacol shown in Chart 2, which results in the formation of two amphiphilic ketones. Thus, in contrast to the amino alcohol and diamine the products should remain water insoluble and amphiphilic and be retained in the interfacial film. Since two simple amphiphiles typically have larger areas/molecule than a single double-chained surfactant, the moderate increase in pressure appears reasonable. Monte Carlo simulations[32] indicate a larger area for a layer of the ketone product amphiphile compared to a layer formed from **5**.

Summary

The results of this study are interesting in several respects. First, as with other studies of surface or interfacial reactions, it is clear that changes in film properties upon reaction represent an effective mode of signal transduction. Thus, in the present study reaction of a very small number of molecules (∼10^{14} molecules or 2×10^{-10} mol) can result in significant decreases or increases in pressure when the photofragmentation reactions are carried out with the films held at constant areas. Although our study suggests that "environmental effects" such as the degree of film compression can modify the observed reactivity, the fact that fragmentation reactions producing either increase or decrease in pressure (due to expansion or contraction as a consequence of the fragmentation) can occur with comparable facility suggests that quite versatile photoinduced electron-transfer reactions may be observable in both intralayer and interfacial modes of reaction. The results obtained in this study suggest that similar photoreactions may be able to produce other mechanical effects and that they may be applicable to a variety of film, polymer, and interfacial environments.

(32) Perlstein, J. *J. Am. Chem. Soc.* **1994**, *116*, 455, 11420.