

of diphenyl ether, then both the intramolecular and the molecular relaxation processes are observed and characterized by Eyring activation parameters.

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Photosensitive Monolayers. Studies of Surface-Active Spiropyran at the Air-Water Interface

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The influence of light on the spreading behavior of three long-chain spiropyran at the air-water interface was investigated. Two compounds were insufficiently polar to spread on the surface of water in the dark and were unstable with respect to crystallization. On 3-5 min of 254-nm irradiation, however, the dispersions spread reproducibly on the surface to give monolayers with typical collapse pressures of 32 mN/m at 0.38 nm²/molecule. Irradiated monolayers of one of the compounds, a thioindolinospiropyran, had high thermal stability. On the other hand, irradiated monolayers of 3',3'-dimethyl-1'-hexadecyl-6-nitrospiro[2*H*-1-benzopyran-2,2'-indoline] (I) revert completely to the surface-inactive starting material by a thermal reaction with a large temperature coefficient. The apparent first-order decay constants for decrease of the surface pressure of I increased from $1.7 \times 10^{-5} \text{ s}^{-1}$ at 11.0 °C to $5.4 \times 10^{-3} \text{ s}^{-1}$ at 46.0 °C, corresponding to an apparent "activation energy" of 144 kJ/mol.

Introduction

The process of vision is an example of a light-induced change in the properties of a bilayer membrane. In this case the photochemical reaction occurs in the protein rhodopsin incorporated into the cell membrane. A number of research groups have worked at creating synthetic photosensitive membranes in which the light-sensitive chromophores are instead part of the surface-active molecules themselves.¹⁻¹⁰ Besides representing an attempt to imitate the process of vision in totally synthetic structures, this research may lead to the development of new photoimaging technology.

Several classes of photoreactions which can lead to pronounced changes in the behavior of membrane-building molecules are illustrated schematically in Figure 1. In the first of these reactions *cis*-*trans* isomerization within the hydrophobic part of the long-chain molecule leads to a change in the packing of the molecules and disruption of the structure of the monolayer or bilayer. A recent example of such a system was described by Kunitake and his co-workers,⁵ who created bilayer vesicles in which one of the membrane components underwent *trans*-*cis* photoisomerization of an azobenzene chromophore. The Japanese group demonstrated that the photoreaction led to appreciable changes in membrane permeability. In another system involving the stilbene chromophore, however, restrictions in molecular mobility within the hydrophobic part of the monolayer were able to suppress the *trans*-to-*cis* photoisomerization completely.⁷

A second type of photoreaction leading to destabilization of a membrane is the photocission reaction illustrated in Figure 1. Subsequent dissolution of the polar head group of a surface-active molecule in the aqueous phase leads to breakdown of the membrane. The photoreactions of monolayers of long-chain α -dia-

zoketones, described by us in a recent publication,⁹ are related to the cleavage reaction depicted in Figure 1. Also in this category is the photochemical reaction of long-chain diazonium salts, described by Fuhrhop et al.⁸

The third type of photoreaction involves a change in the hydrophilicity of the head group. Such a reaction may involve photoionization, as illustrated in Figure 1, or may represent more modest changes in polarity. The photoreactions of anthocyanine dyes containing long hydrocarbon substituents, investigated by Möbius and co-workers,¹⁰ fall into this category. On irradiation of monolayers of these compounds appreciable changes in surface spreading behavior and surface conductivity were observed.

Spiropyran represent another class of compounds which can be used to generate changes in membrane stability by undergoing a change in polarity. These compounds have an additional advantage in the development of light-sensitive membranes because they are photochromic.¹¹ Irradiation of a typical spiropyran

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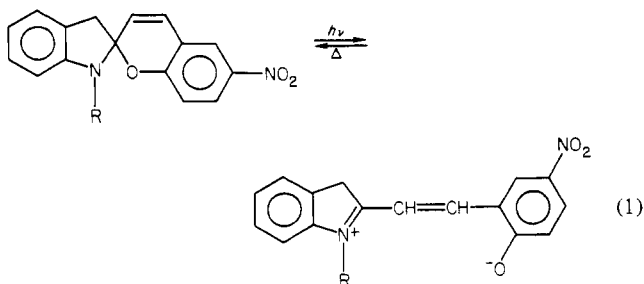
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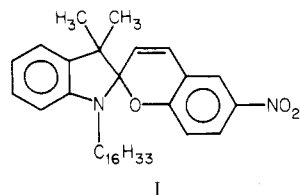
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generates a more polar merocyanine form (eq 1), which reverts



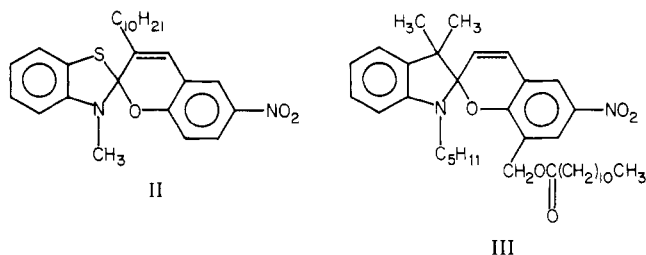
thermally to the starting material with a rate strongly dependent on solvent and temperature. Several authors have investigated the photochromism of spiropyrans in monolayers. Spiropyrans dissolved in poly(methyl methacrylate) monolayers were studied by Blair and Pogue.¹² Rondelez and his co-workers observed better-defined effects on monolayers of copolymers of methyl methacrylate with minor amounts of a spiropyran-containing monomer.¹³ Irradiation with near-UV light produced a 10% increase in the surface pressure at constant surface area.

Long-chain spiropyrans have been synthesized by several groups and investigated in mixed monolayers on water and on glass slides.¹⁴⁻¹⁷ There is great discrepancy between the two published studies. Leblanc's group claimed that the unirradiated form of the long-chain spiropyran I formed normal solid-analogue mono-



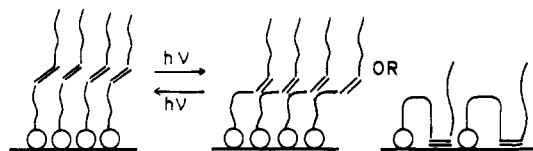
layers on 10^{-3} M sodium phosphate buffer.¹⁷ Polymeropoulos and Möbius reported on the other hand that a spiropyran identical with I except for a slightly longer octadecyl chain on the nitrogen atom failed to give stable monolayers when spread on 2.5×10^{-4} M CdCl₂ buffered with 2.5×10^{-5} M NaHCO₃.¹⁶ Only in 6:1 mixtures of tripalmitoyl glyceride with the spiropyran did the spiropyran give areas per molecule suggesting that it was forming mixed monolayers.

The wide discrepancy between the literature data on long-chain spiropyrans prompted us to conduct further investigations on monolayers of these compounds. The spiropyrans studied were the known compound I and the new compounds II and III, having



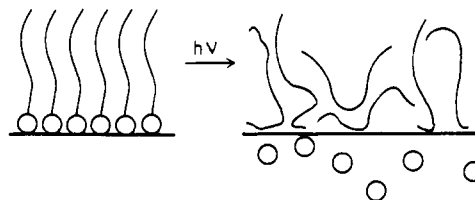
alkyl groups at different positions. Since our goal was to make the changes in surface activity on irradiation as pronounced as

1. CIS-TRANS ISOMERIZATION

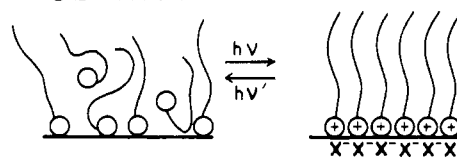


e.g. Kunitake and coworkers, *Chem. Lett.*, 421 (1980).

2. PHOTOCHEMICAL CLEAVAGE



3. CHANGES IN HEAD-GROUP POLARITY



e.g. Möbius et al., *Ber. Bunsenges. Phys. Chem.*, **73**, 845 (1969).

Figure 1. Schematic illustration of several types of photoreactions leading to pronounced changes in the surface activity of amphiphilic compounds.

possible, monolayers of the pure components were investigated. This publication describes the effects of irradiation on these monolayers, as well as the effect of temperature on the rate of the thermal back-reactions from open merocyanine to the closed starting material.

Experimental Section

Materials. 3',3'-Dimethyl-1'-hexadecyl-6-nitrospiro[2*H*-1-benzopyran-2,2'-indoline] (I) was synthesized by the method of Gruda and Leblanc.¹⁵ The compound was purified by column chromatography eluting with chloroform, followed by recrystallization from ethanol, and had a melting point of 84–85 °C (uncorrected). Anal. Calcd for C₃₄H₄₈N₂O₃: C, 76.65; H, 9.08; N, 5.26. Found: C, 76.94; H, 9.18; N, 5.26.

3'-Methyl-3-decyl-6-nitrospiro[2*H*-1-benzopyran-2,2'-benzothiazoline] (II) was obtained by condensation of 3-methyl-2-undecylbenzothiazolinium iodide^{14,18} with 5-nitrosalicylaldehyde in methanol solution in the presence of piperidine. The spiropyran precipitated and was recrystallized from a 4/1 v/v ethanol/benzene solution, mp 90 °C. Anal. Calcd for C₂₆H₃₂N₂O₃S: C, 69.00; H, 7.13; N, 6.29; S 7.08. Found: C, 68.98; H, 7.35; N, 6.13; S, 7.00.

3',3'-Dimethyl-1'-pentyl-6-nitro-8-[(dodecanoyloxy)methyl]-spiro[2*H*-1-benzopyran-2,2'-indoline] (III) was prepared by condensation of 0.01 mol of 3-[(dodecanoyloxy)methyl]-5-nitrosalicylaldehyde with 0.01 mol of 3,3-dimethyl-1-pentyl-2-methyleneindoline in 30 mL of boiling butanone for 2 h. After evaporation of the solvent the precipitate was filtered off, washed with methanol, and recrystallized from ethanol/*n*-hexane (1/1 v/v), mp 83 °C.

The 3-[(dodecanoyloxy)methyl]-5-nitrosalicylaldehyde itself was prepared by reaction of 0.05 mol of 3-(chloromethyl)-5-nitrosalicylaldehyde¹⁹ and 0.06 mol of silver dodecanoate in boiling

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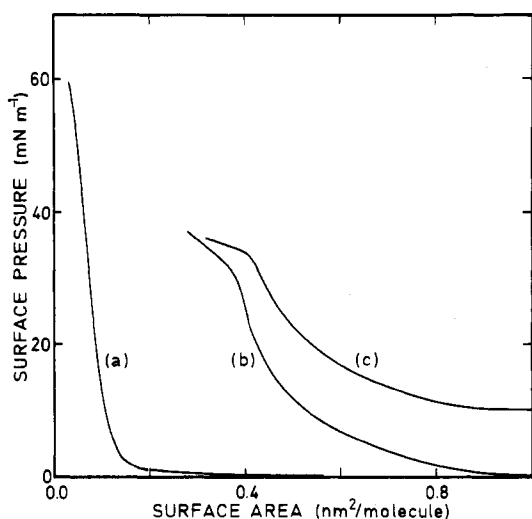


Figure 2. Surface pressure-area curves of films of spiropyran I on pure water: (a) without irradiation, 37.4 °C; (b) after 10 min of 254-nm irradiation in air at 0.65 nm²/molecule, 25.1 °C; (c) irradiated as in (b), 37.4 °C. Curve C is shifted vertically for clarity.

dry benzene for 2 h. The silver halide was filtered off and the yellow filtrate evaporated to dryness. The solid residue was recrystallized from *n*-hexane/benzene (9/1) to give the product in 70% yield.

The spiropyrans were dried under vacuum over phosphorus pentoxide before being weighed, so that no errors in the measured surface areas per molecule were produced by residual solvent or moisture. The solvents chloroform and diethyl ether (Merck, p.a. grade) were used without further purification to spread compounds on the water surface. Deionized water was distilled from alkaline permanganate and then redistilled.

Apparatus. A commercial Langmuir trough (Dr. K. Wolser, MGW Lauda) was altered to hold a 250-mA, low-pressure mercury lamp (Grüntzel, Karlsruhe) in its cover. The lamp was driven by a Grüntzel high-voltage power supply at a current of 100 mA. Temperature control of the aqueous subphase was provided by a Lauda Model K4R constant-temperature bath and circulating pump.

Compounds were spread from dilute (1 mg/mL) solutions in chloroform or ether on the surface of pure unbuffered water (pH 6). All manipulations of unirradiated solutions and measurements on unirradiated films were carried out with the room lights off, in order to minimize interference from merocyanine photoproducts. Surface pressure-area diagrams of monolayers irradiated in air and monolayers irradiated after 45-min purging of the trough with nitrogen were compared. As the curves were almost identical, all subsequent experiments were carried out in air. For the generation of surface pressure-area diagrams, films were irradiated for 10 min at a constant area of 0.65 nm²/molecule and then compressed at a speed of 0.05 nm² molecule⁻¹ min⁻¹ with the lamp on. For kinetic measurements on monolayers, a film was irradiated at a constant area of 0.50 nm²/molecule until the surface pressure had reached its maximum value. The lamp was switched off and the decay of the surface pressure recorded continuously on a BBC Goetz X-Y-t recorder.

Results and Discussion

Effect of Irradiation on Spreading Behavior. Figure 2 shows the surface pressure-area diagrams of the long-chain spiropyran I on water, both before irradiation and after 254-nm irradiation for 10 min in air. Since the unirradiated film exerts no pressure on the measuring barrier above a surface area of 0.20 nm²/molecule, corresponding to closest packing of the alkyl chains, it is clear that this spiropyran does not form monolayers on pure water. Identical results were obtained by using chloroform or ether as the spreading solvent. The high surface pressure reached at about 0.05 nm²/molecule arises because the spiropyran is unstable with respect to formation of crystals on the water surface, and

Scheme I

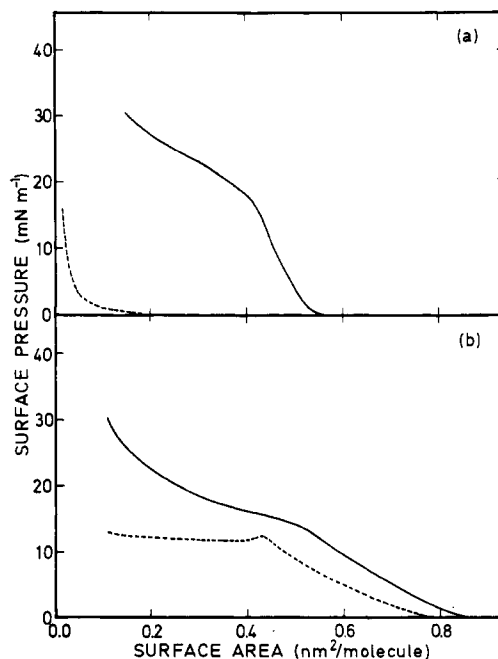
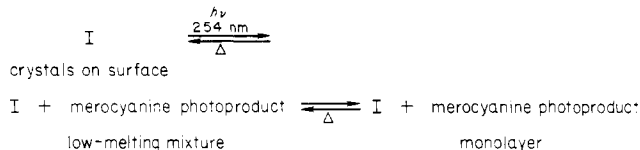


Figure 3. (a) Surface pressure-area curves of films of spiropyran II on pure water: (---) without irradiation, 28.5 °C; (—) after 10 min of 254-nm irradiation in air at 0.65 nm²/molecule, 30.0 °C. (b) Surface pressure-area curves of films of spiropyran III on pure water, 21.8 °C: (---) without irradiation; (—) after 10 min of 254-nm irradiation in air at 0.65 nm²/molecule.

these crystals resist compression at very small surface areas. This failure of I to give monolayers in the dark contradicts the results of Morin et al.,¹⁷ which suggested that the compound gave monolayers containing closest-packed alkyl chains. It is difficult to visualize how such closest packing could occur, when Polymeropoulos and Möbius estimate the surface area of the spiropyran ring system to lie between 0.4 and 0.5 nm²/molecule.¹⁶

On the other hand, irradiation of these films on the surface does give stable monolayers. These have reproducible inflection points around 0.40 nm²/molecule, values more in line with the large size of the spiropyran ring system. The compressed films are a deep blue oil, whereas the unirradiated films form colorless crystalline rafts on the surface. Scheme I illustrates the proposed mechanism of spreading of the irradiated compound. Since the spreading is thermally reversible and since both open and closed forms have high absorptions at the irradiation wavelengths,¹⁵ the monolayers must contain both products. Thus, the spreading mechanism is more complex than the complete conversion of an inactive isomer into a more polar one. Mixed crystals of product and starting material may cease to be more stable thermodynamically than mixed monolayers, so that the product mixture disperses over the surface. That the open merocyanine form is highly polar is known from the effects of solvent on its absorption spectrum²⁰ and is substantiated by recent luminescence measurements and semi-empirical calculations.²¹

Compound II shows behavior similar to that of spiropyran I (Figure 3). Before irradiation no monolayers are formed, while after irradiation a monolayer with a poorly defined inflection point

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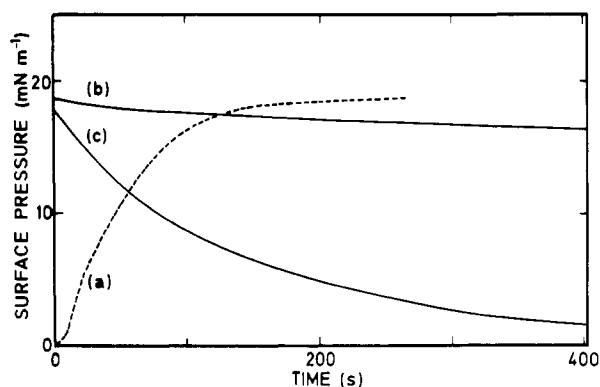


Figure 4. Change of surface pressure with time for films of spiropyran I at a constant area of $0.50 \text{ nm}^2/\text{molecule}$: (a) during 254-nm irradiation, 46.3°C ; (b) during thermal relaxation, 20.0°C ; (c) during thermal relaxation, 46.3°C .

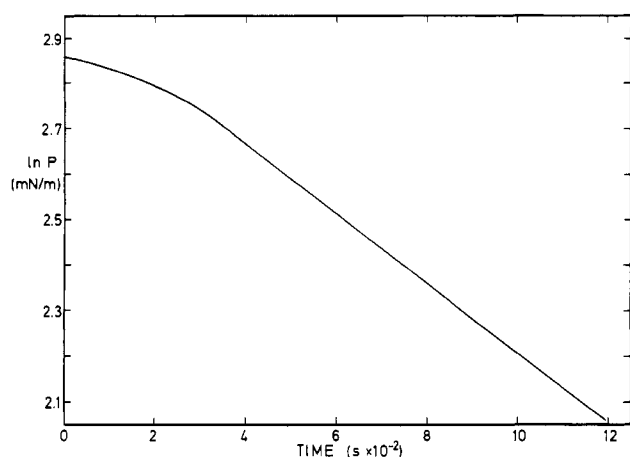


Figure 5. Change of surface pressure with time for monolayers of irradiated I at a constant area of $0.50 \text{ nm}^2/\text{molecule}$, 28.8°C . Data replotted according to a first-order rate equation.

at 18 mN/m and $0.40 \text{ nm}^2/\text{molecule}$ is observed. The fact that sharp collapse points are not displayed by this system is probably a consequence of the large surface area of the zwitterionic head group and the short alkyl chain. The balance between monolayer stability and crystal formation is fairly critical: unlike the other two spiropyrans, III forms stable monolayers both in the dark and on irradiation, as shown in Figure 3.

Studies of the Rate of Formation and Collapse of Merocyanine Monolayers. Figure 4 illustrates the change in surface pressure with time of spiropyran films, both when the lamp is turned on and after it is turned off. During irradiation the surface pressure rises after a short induction period to a constant value with a half-reaction time of 44 s, only slightly affected by temperature. In the case of II the surface pressure remains almost constant at all experimental temperatures when the lamp is switched off. Monolayers of I show completely different behavior: the rate of thermal relaxation of the surface pressure increases strongly with increasing temperature.

In Figure 5 the thermal relaxation of the surface pressure P for monolayers of irradiated I is replotted according to eq 2.

$$-\ln P = kt + \text{constant} \quad (2)$$

After a short induction time the decay of the surface pressure settles into single exponential decay. From the linear portion of the decay curves measured at various temperature, rate parameters k were obtained and plotted against temperature according to the Arrhenius equation, as shown in Figure 6. The decay data measured at 46.0°C are the least accurate because of the rapid rate of evaporation of water from the surface as well as the contamination of the surface by impurities carried by condensing

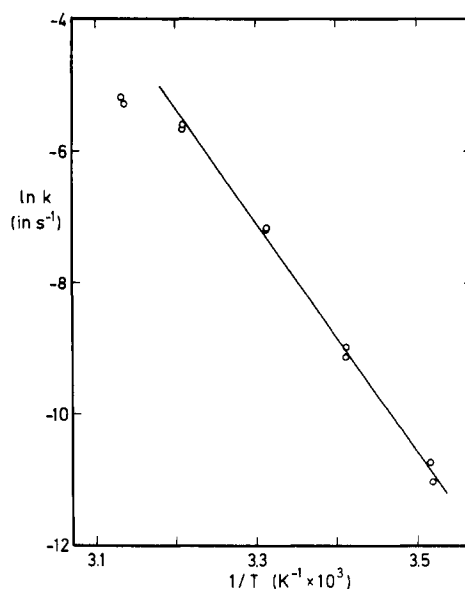
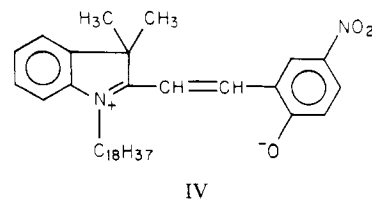


Figure 6. Variation of first-order rate constant k for decay of surface pressure of monolayers of irradiated I with temperature T . The slope of the straight line corresponds to a temperature coefficient of 144 kJ/mol .

moisture. With the exception of the data obtained at this high temperature, the decay of the surface pressure does show pseudo-Arrhenius behavior, with a temperature coefficient of 144 kJ/mol .

It must be stressed that these rate parameters and "activation energy" are for the relaxation of the surface pressure, and so are only indirectly related to the thermal conversion of merocyanine to starting spiropyran taking place in the monolayers. For the rate measurements to refer directly to the chemical reaction, the surface pressure would have to be proportional to the surface concentration of photoproduct. Nevertheless, Polymeropoulos and Möbius have measured a first-order rate constant of $2.7 \times 10^{-4} \text{ s}^{-1}$ (at the temperature of the sample compartment of their UV spectrometer) for the fading of IV dispersed in tripalmitoyl gly-



ceride on glass supports.¹⁶ This value is very close to the interpolated value of $3.3 \times 10^{-4} \text{ s}^{-1}$ at 25.0°C which we obtain from surface pressure measurements on monolayers of the irradiated spiropyran I and suggests that the decay of the surface pressure follows the chemical isomerization closely.

Typical activation energies for the thermal conversion of photoisomer to starting spiropyran range from 65 to 100 kJ/mol for spiropyrans in homogeneous solution, depending on solvent polarity.^{20,22,23} The relaxation of the surface pressure of irradiated I is the result of at least two processes, namely, the conversion of the merocyanine to the starting compound, followed by the transfer of the spiropyran from the monolayer on the surface to the bulk crystalline phase. The extra step of removal of a molecule from the monolayer may explain why the temperature coefficient for relaxation of the surface pressure is higher than the activation energies of decoloration of spiropyrans in solution. On the other hand, the higher activation energy for the isomerization on the water surface could also be a natural progression in the increase

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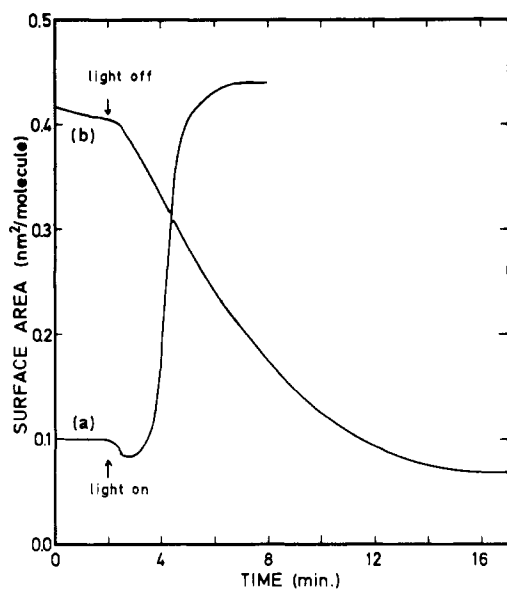


Figure 7. Variation of surface area of films of spiropyran I at constant pressure P : (a) during irradiation at $P = 10$ mN/m, 14.8 °C; (b) during thermal relaxation at $P = 20$ mN/m, 38.5 °C.

of activation energy with solvent polarity.

Measurements at Constant Pressure. Figure 7 shows the change in surface area which occurs when a collapsed crystalline dispersion of spiropyran I on water is irradiated at a constant

surface pressure of 10 mN/m. Although the measuring head and the movable barrier of the film balance block off a large fraction of the light, the irradiated film forms a monolayer on the surface and gradually pushes the barrier back to a final area of 0.45 nm²/molecule. When the lamp is switched off, the barrier slowly pushes the film back as the thermal back-reaction proceeds.

Conclusions

The literature contains several examples of monolayer systems which are photochemically active. Without exception the changes in the surface activity produced by these photochemical reactions are relatively small, corresponding to surface pressure changes $(\Delta P/P)_A$ and surface area changes $(\Delta A/A)_P$ on the order of 10–20%.^{10,13,16} The present article described a reversible and an irreversible photochemical conversion of a surface-inactive system into a surface-active one. In this system $(\Delta P/P)_A = \infty$ and $(\Delta A/A)_P = 400\%$. The spiropyrans I and II thus constitute and particularly effective examples of photosensitive surface-active systems.

Acknowledgment. D.A.H. thanks the Alexander von Humboldt-Stiftung for the award of a research fellowship (1981–1982).

Registry No. I, 60168-17-4; II, 88271-60-7; III, 88253-63-8; 3-methyl-2-undecylbenzothiazolinium iodide, 88253-64-9; 5-nitrosalicylaldehyde, 97-51-8; 3-[(dodecanoyloxy)methyl]-5-nitrosalicylaldehyde, 88253-65-0; 3,3-dimethyl-1-pentyl-2-methyleneindoline, 88253-66-1; 3-(chloromethyl)-5-nitrosalicylaldehyde, 16644-30-7; silver dodecanoate, 18268-45-6.

Electron Density and Bond Polarization Effects in Reactions of Energetic Carbon-11 Leading to Acetylene

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Evidence is presented indicating that reactions of energetic carbon-11 are effected by the presence and type of halogen in gas-phase methyl halides. Correlations of acetylene-¹¹C yields with ¹H and ¹⁹F NMR chemical shifts of the substrates indicate that electron density and bond polarization factors influence the mechanism(s) leading to hot products such as (¹¹C)₂H₂. (¹¹C)₂H₂ was formed primarily by an intramolecular mechanism in methyl chloride.

Introduction

How reactions by electrophilic carbon-11 intermediates¹ (C, C₂, CH, C₂H, etc.) with a C–H bond are affected by the presence of a halogen is not clearly understood. Wolf and his co-workers^{2–4} have noted bond energy effects in the formation of acetylene-¹¹C in substituted ethane derivatives. Attack of energetic ¹¹C atoms at C–H bonds (most likely carbon insertion, stripping, or abstraction) is very much favored over carbon-11 attack leading to insertion into the C–F bond.^{5,6} We investigated the reactions

of energetic ¹¹C in halogen-substituted methane derivatives.⁷ This article reports an apparent electron density and bond polarization effects that appear to affect the course of reactions leading to the formation of acetylene-¹¹C.

Experimental Section

The ¹²C(p,pn)¹¹C and the ¹⁶O(p,pn⁴He)¹¹C nuclear reactions were induced with 33-MeV protons at the BNL 60-in. cyclotron. All reaction systems were at a total pressure of 760 torr with 34 torr of oxygen present. The 4.5% O₂ acted as an effective sca-

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