and that nucleophilic catalysis at one of the retinoid carbons will be important. Two biological molecules have been reported capable of isomerizing the retinals, and both almost certainly do so by mechanisms very similar to, if not identical with, those described here. Although no mechanism was suggested, it has been found that reduced flavins are potent catalysts of the isomerization of *all-trans*-retinal to 13-*cis*- and 9-*cis*-retinal.[20] As this work was completed before the advent of HPLC and before it was appreciated that 11-*cis*-retinal was only represented to the extent of 0.1% at equilibrium, it now seems clear that reduced flavins rapidly bring the retinals to equilibrium. Based on what is now known about secondary amine catalysts, the mechanism shown in Scheme VI is suggested for the catalytic potency of the reduced flavins. Interestingly, when this reaction was carried out in tritium water, no tritium incorporation was detected in the retinals.[20] This again argues against the possibility of an enolization mechanism in the isomerization reaction. A second biomolecular system which can effect the catalyzed isomerization of the retinoids is phosphatidylethanolamine (PE). In an aqueous environment PE has the added advantage of sequestering the retinal and bringing it into apposition with the amino group of the lipid, thus ensuring rapid and specific Schiff base formation.[21] It has been suggested that the phosphate oxygen could act as a nucleophile in these isomerization reactions.[21] These observations open up the possibility that small biological molecules could be the endogeneous catalysts for vitamin A aldehyde isomerization in vivo and that the mechanism of isomerization could be quite similar to that reported here.

Acknowledgment. We thank Dr. William. E. Scott of Hoffmann-LaRoche Inc., Nutley, NJ, for the generous supplies of 11-*cis*-, 13-*cis*-, and 9-*cis*-retinal. This work was supported by the National Institutes of Health Grant No. EY-04096.

Registry No. 11-*cis*-retinal, 564-87-4; 13-*cis*-retinal, 472-86-6; 9-*cis*-retinal, 514-85-2; 11-*cis*-retinal aniline Schiff base, 90696-42-7; 11-*cis*-retinal butylamine Schiff base, 52647-48-0; 13-*cis*-retinal butylamine Schiff base, 51847-39-3; 9-*cis*-retinal butylamine Schiff base, 51804-54-7; 11-*cis*-retinal piperidine perchlorate Schiff base, 90696-44-9; $H_2NOH\cdot HCl$, 5470-11-1; $C_5H_{11}N\cdot HClO_4$, 57367-18-7; $BuNH_2$, 109-73-9; $PhNH_2$, 62-53-3; $C_5H_{11}N$, 110-89-4.

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Photosensitive Monolayers. Photochemistry of Long-Chain Diazo and Azide Compounds at the Air–Water Interface

David A. Holden,* Helmut Ringsdorf, and Michael Haubs

Contribution from the Institut für organische Chemie, Universität Mainz, Postfach 3980, D-6500 Mainz, West Germany. *Received January 6, 1984*

Abstract: The photochemistry of a number of surface-active diazo and azide compounds was investigated in monolayers at the air–water boundary. Irradiation of long-chain α-diazo ketones with ultraviolet light leads to rapid loss of nitrogen. The resulting ketenes react with the subphase to generate carboxylic acids (photochemical Arndt–Eistert reaction) and dimerize to give β-lactones as side products. A long-chain diester of 2-diazopropanedioic acid loses nitrogen and adds water, yielding the diester of 2-hydroxypropanedioic acid. α-Azido ketones split off nitrogen and the resulting isocyanates react with water (photochemical Curtius reaction) and undergo further degradation to give complex product mixtures. These reactions lead to pronounced changes in the spreading behavior of the monolayers. Depending on functional group, chain length, substrate pH, and temperature it is possible to achieve changes in compressibility and collapse pressure, disappearance of expanded phases, collapse of monolayers to give oily films, or disappearance of monolayers by dissolution in the subphase.

Introduction

Photoreactions in thin films are the basis of important industrial processes, including photolithography and photoresist technology.[1] In an effort to achieve still higher resolution, and possibly even to store binary information at the molecular level, the extension of these photoreactions to Langmuir–Blodgett monolayers has been suggested.[2] Other reasons for the present worldwide interest in the chemistry of surface-active molecules arise from the links to the processes of vision and photosynthesis. In addition, membranes whose properties are affected by photochemical reactions may find applications in photography and solar energy conversion.[3]

In general several types of chemical reactions might be expected to create pronounced changes in monolayer or membrane properties[4]: cis–trans isomerization within the hydrophobic chains of an amphiphilic molecule,[5] splitting of the hydrophilic head group away from the hydrocarbon chain,[6] reactions which cause large changes in the polarity of the head group,[7] dimerization,[8] or polymerization.[9] In a recent publication dealing with photochemistry in monolayers, surface-active spiropyrans were described

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*Present address: Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1.

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which showed dramatic changes in spreading behavior on irradiation.[4] The photoreactions of these spiropyrans were examples of the third class of reaction, of an isomerization which led to an increase in head-group polarity and the stabilization of monolayers. The changes in spreading behavior were particularly prominent because the photosensitive compounds were the building blocks of the monolayers and were not simply chromophores dissolved in a photochemically inert membrane.

The present publication illustrates examples of the photochemical reactions of long-chain compounds containing diazo ketone and azido ketone groups. These reactions lead subsequently to a wide range of changes in monolayer properties, including the destabilization of a surface film. The photochemistry of small-molecule diazo ketones and azido ketones has been extensively investigated in homogeneous solution,[10,11] but little has been done to extend this work to interfaces. Horner and Schwarz described the synthesis of 4-octadecylbenzazide and 1-(4-octadecylphenyl)-2-diazo-1-oxoethane, as well as attempts to build up multilayers of these substances on glass slides.[12] The synthesis of analogues of fatty acids containing azide and diazo groups in their hydrophobic parts was recently achieved, and it was observed that these long-chain compounds were incorporated by the microorganism E. coli into its membrane material.[13,14] Cholesteryl diazoacetate was recently synthesized for use in studies of the labeling of biological membranes.[15] Besides constituting interesting examples of systems where photochemistry has an effect on interfacial phenomena, surface-active compounds containing reactive functional groups such as the diazo ketones and azido ketones described in the present work may find applications in modifying solid surfaces.[16]

Experimental Section

Melting points were recorded on a Büchi immersion apparatus and are uncorrected. All photosensitive compounds were prepared in dim light and were stored in the dark at −20 °C.

Materials. Tetradecanoic (Fluka), octadecanoic (Merck), eicosanoic (EGA), octacosanoic (Fluka, puriss.), and oleic acids (Fluka) were of 99% purity or more and were used in subsequent syntheses without further purification.

Tetradecanoyl Chloride.[17] Twenty-five grams of tetradecanoic acid, 10 mL of thionyl chloride, 10 mL of CH_2Cl_2, and 2 drops of *N*,*N*-dimethylformamide were stirred at 40 °C for 8 h with protection from atmospheric moisture. The CH_2Cl_2 and unreacted $SOCl_2$ were removed on the rotary evaporator, and the acid chloride was fractionally distilled under high vacuum. Other acid chlorides were obtained similarly, except that eicosanoyl, octacosanoyl, and oleyl chlorides were used immediately without distillation.

1-Diazo-2-oxononadecane.[18] A dilute solution of diazomethane in ether was prepared by a standard procedure.[19] To excess CH_2N_2 in ether at 0 °C a solution of 2 g of octadecanoyl chloride in dry ether was added dropwise with stirring. After the mixture was stirred for 2 h in the dark at 0 °C the solvent was evaporated and the solid was recrystallized twice from 150 mL of ethanol between 35 and −20 °C. Three further recrystallizations from *n*-hexane between 30 and −20 °C were necessary to remove all traces of an impurity, probably 1-chloro-2-oxononadecane,[18] having an IR carbonyl band at 1730 cm^{-1}. The product forms pale yellow crystals; mp 67–67.5 °C; IR (Nujol) 3090 cm^{-1} (unsaturated CH stretch), 2110, 2130 ($C{=}N{=}N$ stretch), 1625 ($C{=}O$ stretch of conjugated ketone); ^1H NMR (Jeol 60 MHz, $CDCl_3$) δ 0.90 (t, 3 H), 1.27 (m, 30 H), 2.30 (t, 2 H), 5.23 (s, 1 H); UV (hexane) λ_{max} 377 (ϵ 18.2 $M^{-1}\,cm^{-1}$), 245 nm (12 900). The extinction coefficient at 254 nm is 10 500 $M^{-1}\,cm^{-1}$; TLC (silica gel, THF eluant) one spot, R_f 0.9. Anal. Calcd for $C_{19}H_{36}N_2O$: C, 73.97; H, 11.76; N, 9.08. Found: C, 73.94; H, 11.64; N, 8.92.

In a similar manner 1-diazo-2-oxopentadecane (mp 53.5–54.0 °C), 1-diazo-2-oxoheneicosane (mp 69–70 °C), 1-diazo-2-oxononacosane (mp 85–86 °C) and *cis*-1-diazo-2-oxo-10-nonadecene (liquid at room temperature) were synthesized, with satisfactory IR, NMR, and UV spectra and elemental analyses.

Dioctadecyl Propanedioate.[20] Octadecyl alcohol was prepared by $LiAlH_4$ reduction of 99% octadecanoic acid in refluxing ether.[21] The free alcohol was liberated by overnight stirring of the ether solution over powdered $Na_2SO_4\cdot 10H_2O$. A solution of 3.9 g of 1-octadecanol in 20 mL of dry dichloromethane was purged with nitrogen and cooled to 0 °C. Malonyl dichloride (Aldrich), 1.01 g, was added all at once and then 1.79 g of dry *N*,*N*-dimethylaniline was added dropwise with stirring over 30 min. After overnight stirring the solution was refluxed briefly, diluted to 130 mL with CH_2Cl_2, and allowed to cool. The organic solution was extracted with 1 M HCl, washed neutral with water, and dried over Na_2SO_4. After removal of the solvent the product was recrystallized from ethanol. The yield of off-white crystals was 3.3 g (75%): mp 62–62.5 °C; IR (Nujol) 1740, 1710 cm^{-1} (split ester $C{=}O$ band).

Dioctadecyl 2-Diazopropanedioate.[22] A solution of 1.4 g of *p*-toluenesulfonyl azide,[23] 0.74 g of dry triethylamine, and 3.1 g of recrystallized dioctadecyl propanedioate in 15 mL of dry CH_2Cl_2 was refluxed gently for 19 h. Another 1 g of azide was added, and refluxing was continued for another 9 h. Cooling the reaction mixture to 0 °C produced crystals. These were filtered off and recrystallized twice from CH_2Cl_2 between 25 °C and −20 °C to give 1.7 g (53%) of very pale yellow crystals: mp 63–64 °C; IR (Nujol) 2160 ($C{=}N{=}N$), 1680 cm^{-1} ($C{=}O$ of ester); NMR ($CDCl_3$) δ 0.90 (t, 6 H), 1.27 (m, 64 H), 4.30 (t, 4 H); UV (hexane) λ_{max} 351 (ϵ 21 $M^{-1}\,cm^{-1}$), 250 nm (8200). The extinction coefficient at 254 nm is 7700 $M^{-1}\,cm^{-1}$. Anal. Calcd for $C_{39}H_{74}N_2O_4$: C, 73.77; H, 11.95; N, 4.41. Found: C, 73.71; H, 11.74; N, 4.35.

4-Octadecyloxybenzoic Acid.[24] A solution of 20 g of 4-hydroxybenzoic acid (Aldrich), 48.2 g of 1-bromooctadecane (Merck), 20 g of KOH, and 0.1 g of KI in 150 mL of 85% ethanol was refluxed for 48 h. Most of the solvent was evaporated under reduced pressure, and the solid was treated with 500 mL of water containing 25 mL of concentrated HCl. The solid was filtered by suction, washed with water, and dried in vacuo. It was then recrystallized from chloroform to give flaky crystals: mp 101–102 °C to an oily liquid-crystalline phase (lit.[24b] mp 102 °C to smectic phase); IR (Nujol) 3000 cm^{-1} (OH of acid).

4-Octadecyloxybenzoyl Azide[12] (1). Ten grams of 4-octadecyloxybenzoic acid were stirred with 50 mL of thionyl chloride for 18 h and the excess $SOCl_2$ was removed at reduced pressure. The acid chloride (6.94 g) was dissolved in a mixture of 50 mL of acetone and 100 mL of THF and cooled to 0 °C, and a solution of 21.5 g of NaN_3 in 25 mL of water was added dropwise over 1 h. The reaction mixture was stored at 0 °C for 10 days and then diluted with water. The product was extracted with CH_2Cl_2, and the combined organic extracts were dried over Na_2SO_4. After removal of the solvent the product was recrystallized twice from ether between 30 °C and −20 °C to yield 5.5 g (78% from the acid chloride) of a white solid: mp 56–57 °C; IR (Nujol) 2150 (N_3 group), 1690 cm^{-1} ($C{=}O$); NMR ($CDCl_3$) δ 0.9 (t, 3 H), 1.3 (m, 32 H), 3.97 (t, 2 H), 6.8–8.0 (m, 4 H); UV (cyclohexane) λ_{max} 289 (ϵ 22 400 $M^{-1}\,cm^{-1}$), 284 (25 500), 277 nm (24 310). The extinction coefficient at 254

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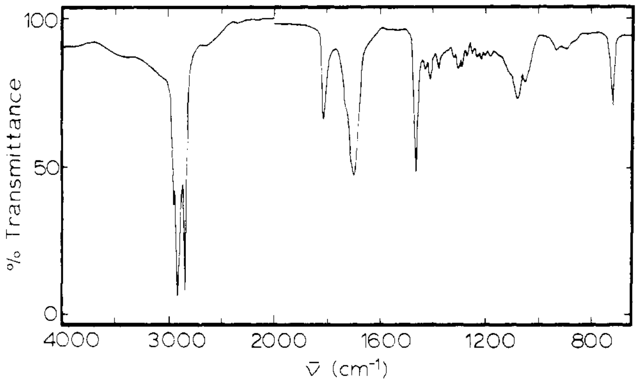

Figure 1. Infrared spectrum (KBr) of the photoproduct obtained from 90 s of 254-nm irradiation of monolayers of 1-diazo-2-oxononadecane on water.

nm is 8360 M^{-1} cm^{-1}. Anal. Calcd for $C_{25}H_{41}N_3O_2$: C, 72.25; H, 9.94; N, 10.11. Found: C, 72.10; H, 9.83; N, 10.10.

1-(4-(Octadecyloxy)phenyl)-2-diazo-1-oxoethane[12] (2). A solution of 1.14 g of 4-(octadecyloxy)benzoyl chloride in 20 mL of CH_2Cl_2 was added dropwise to excess diazomethane in ether at 0 °C. After the mixture was stirred 40 min the solvent was evaporated at reduced pressure. The product was recrystallized twice from 1:1 CH_2Cl_2–hexane between 30 °C and −20 °C to give 0.53 g (46%) of fine yellow crystals: mp 79.5–80 °C; IR (Nujol) 3085, 2130, 1610 cm^{-1}; NMR ($CDCl_3$) δ 0.9 (t, 3 H), 1.3 (m, 32 H), 4.13 (t, 2 H), 5.97 (s, 1 H), 7.0–8.0 (m, 4 H); UV (cyclohexane) λ_{max} 375 (ϵ 36.3 M^{-1} cm^{-1}), 286 nm (22 400). The extinction coefficient at 254 nm is 8980 M^{-1} cm^{-1}. Anal. Calcd for $C_{26}H_{42}N_2O_2$: C, 75.32; H, 10.21; N, 6.76. Found: C, 75.23; H, 10.23; N, 6.49.

The Langmuir trough and techniques for irradiation of monolayers were described in a previous publication.[4] Solutions were spread from chloroform on the surface of pure water or 0.01 M NaOH. Fresh $CHCl_3$ solutions were prepared daily.

Preparative Photoreaction of Monolayers of 1-Diazo-2-oxononadecane on Water. The surface-active compound was spread over the entire aqueous surface (700 cm^2) below the low-pressure mercury lamp. Monolayers were irradiated at 254 nm for 90 s in air at 14.5 °C at areas of 0.23 nm^2/molecule, corresponding to a surface pressure of 0.0 mN m^{-1}. The surface area was decreased to a 0.5-cm strip, and the monolayers were transferred to a previously unused glass vial with a clean metal spatula. A total of 12 monolayers were collected and dried in vacuo over P_4O_{10}. The product is a colorless solid, mp 59–62 °C. Its infrared spectrum in KBr is shown in Figure 1. In order to eliminate the IR peaks of water, the KBr was dried in vacuo over P_4O_{10} at 100 °C, a tray of P_4O_{10} was kept in the sample compartment of the IR spectrometer, and the spectrum was recorded against a KBr reference pellet. MS of photoproduct (main peaks only): m/z 560 (relative intensity 4), 289 (30), 281 (23), 267 (13), 129 (24), 112 (22), 111 (18), 99 (11), 98 (100), 84 (24), 73 (52), 71 (47), 69 (39), 60 (44), 57 (82), 55 (56), 43 (88), 41 (44). The irradiation and analysis of other compounds were similar, except that the temperature of the aqueous subphase was adjusted to ensure that the photoproduct was a solid easily removed from the surface.

Photoproduct from irradiation of dioctadecyl 2-diazopropanedioate monolayers: white solid; mp 53.5–57.5 °C; IR (KBr) 3300, 2930, 2860, 1750, 1475, 1290, 1250, 1140, 730 cm^{-1}; MS, m/z 624 (8), 581 (11), 580 (26), 501 (21), 455 (16), 372 (10), 357 (9), 328 (21), 313 (14), 297 (14), 253 (10), 97 (14), 83 (14), 71 (14), 69 (11), 58 (100), 55 (15), 43 (16), 41 (13).

Photoproduct from irradiation of monolayers of 1: brown solid, does not melt sharply; IR (KBr) 3300, 3220, 2930, 2860, 1660, 1615, 1520, 1475, 1260, 1175, 1040, 850, 730 cm^{-1}; MS, m/z 748 (2), 734 (8), 733 (13), 718 (9), 657 (3), 403 (10), 402 (32), 390 (20), 389 (14), 388 (4), 387 (10), 374 (14), 373 (48), 362 (8), 361 (31), 360 (3), 359 (4), 358 (3), 151 (17), 150 (100), 139 (27), 138 (54), 137 (50), 135 (47), 121 (53), 109 (80), 97 (29), 85 (24), 83 (39), 71 (43), 69 (50), 57 (98), 55 (64).

Photoproduct from irradiation of monolayers of 2: colorless solid; mp 67–70 °C; IR (KBr) 3080 (broad), 2930, 2860, 1705, 1610, 1520, 1475, 1265, 1180, 840, 730 cm^{-1}; MS, m/z 404 (27), 153 (12), 152 (100), 138 (14), 107 (57), 83 (11), 71 (15), 69 (17), 57 (33), 55 (23), 43 (24), 41 (11).

Results and Discussion

Scheme I

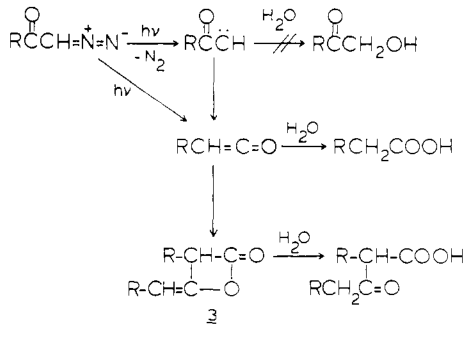

Table I. Ratio of Peak Heights of IR C═O Bands of Ketene Dimer and Carboxylic Acid in Product Mixtures from UV Irradiation of Diazo Ketone Monolayers on H_2O

compound	I_{dimer}/I_{acid}
1-diazo-2-oxopentadecane	0.97
1-diazo-2-oxononadecane	0.65
1-diazo-2-oxoheneicosane	0.32
1-diazo-2-oxononacosane	0.10
diazo ketone **2**	0.00

Products of Photoreactions in Monolayers. Figure 1 illustrates the IR spectrum of the photoproduct mixture obtained from UV irradiation of monolayers of 1-diazo-2-oxononadecane on water. The sharp band at 3090 cm^{-1}, corresponding to the C–H stretch of the unsaturated carbon atom of the diazo group, the C═N═N bands at 2110 and 2130 cm^{-1}, and the 1625-cm^{-1} band of the conjugated ketone are all absent from the product spectrum. Instead there are new carbonyl bands at 1720 and 1827 cm^{-1} and a broad OH band centered at 3100 cm^{-1}.

The mass spectrum of the photoproduct mixture shows a molecular ion peak at m/z 298 corresponding to nonadecanoic acid, a fragmentation pattern typical of a long alkyl chain, and a moderately strong peak at m/z 60 corresponding to loss of $CH_2{=}C(OH)_2^+$. In addition a molecular ion peak at m/z 560 is observed, a mass which corresponds to the dimer of the ketene formed by splitting off of nitrogen in the monolayer.

Scheme I summarizes the photochemistry of the long-chain diazo ketones in monolayers. These compounds undergo a photochemical analogue[25] of the Arndt–Eistert reaction.[18] In addition to the OH band at 3100 cm^{-1} and the C═O peak at 1720 cm^{-1}, the infrared spectrum of the products from the C_{21} and C_{29} diazo ketones show complex splitting of the C–O band centered at 1250 cm^{-1}, behavior characteristic of solid straight-chain carboxylic acids.[26] Further evidence besides the IR and MS spectra for the formation of the acid is found in the high solubility of the monolayers formed by irradiation of 1-diazo-2-oxopentadecane on 0.01 M NaOH. This fact and the absence of an OH band at 3300 cm^{-1} show that the product is the carboxylic acid formed by addition of water to the ketene and not an α-hydroxy ketone which would be formed by direct addition of water to an α-keto carbene.

The IR band at 1827 cm^{-1} and the MS peak at m/z 560 are evidence for formation of the unsaturated β-lactone **3** through dimerization of the ketene. Although the anhydride of a carboxylic acid could give a similar IR band,[26] it is unlikely that the conditions of irradiation and product collection would leave the anhydride functional group intact. Further evidence for the formation of ketene dimer is the presence of a small amount of its hydrolysis product, the β-keto acid shown in Scheme I. In the case of the C_{15} diazo ketone, this gives rise to a peak in the mass spectrum at m/z 466/467.

Table I lists the relative intensities of the IR C═O bands of acid and ketene dimer for the long-chain diazo ketones. The aromatic diazo ketone **2** does not form any β-lactone dimer. Within the homologous series of aliphatic diazo ketones, the yield of ketene dimer decreases with increasing chain length. Di-

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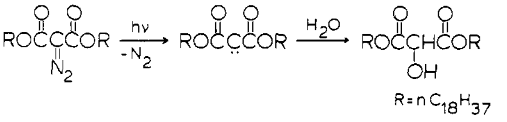
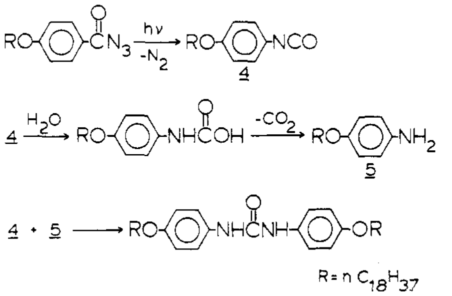
Scheme II



Scheme III



merization of the ketene in a monolayer requires movement of the alkyl chain through the monolayer, and this mobility is hindered as the alkyl chains are lengthened.[27] The results of Table I are an interesting example of the effect of molecular mobility on the course of a reaction in a monolayer.

The photochemistry of monolayers of dioctadecyl 2-diazopropanedioate, shown in Scheme II, is straightforward. The product IR spectrum shows loss of the diazo group absorption at 2160 cm^{-1}, a shift of the carbonyl band to 1750 cm^{-1}, and the appearance of a broad OH band at 3300 cm^{-1}. The molecular ion at m/z 624 and the fragmentation pattern are characteristic of the dioctadecyl ester of 2-hydroxypropanedioic acid. In this reaction the addition of water to the carbene is able to complete with rearrangement reactions of the carbene.[28]

Only the photochemistry of the long-chain azido ketone **1** is more complex. The product IR spectrum shows loss of the azide absorption and the formation of an amide C=O band at 1660 cm^{-1} and NH bands at 3220 and 3300 cm^{-1}. The mass spectrum shows molecular ion peaks at m/z 749 and 361, corresponding to the urea derivative and the aromatic amine, respectively, shown in Scheme III. The fragmentation pattern of the photoproducts from **1** differs from those of the aliphatic compounds in the fact that the positive charge tends to remain on the aromatic ring, so that the breakup of the hydrocarbon chain is less apparent. This system is an example of the photochemical Curtius reaction.[10,29] Unlike the other reactions investigated in monolayers, the products of irradiation of the azide **1** also absorb strongly at 254 nm so that secondary photoreactions are difficult to avoid. In particular the further photooxidation of 4-(octadecyloxy)aniline may explain why the product monolayers are invariably colored brown.[30]

Effect of Photoreaction on Spreading Behavior. The irradiation of monolayers of diazo and azide compounds on water causes pronounced changes in their spreading behavior. Figure 2 shows the surface pressure–area curves of monolayers of 1-diazo-2-oxopentadecane on pure water, both before and after 60 s of 254-nm irradiation. The unirradiated film shows an expanded phase between 0.20 and 0.50 nm^2/molecule at all temperatures above 4 °C, whereas the irradiated film shows only a closest-packed phase below 12 °C, with a collapse area of 0.20 nm^2/molecule. Irradiation of a monolayer of 1-diazo-2-oxopentadecane between 4 and 10 °C thus leads to a phase transition within the monolayer. The collapse areas of the diazo ketones are close to the cross-sectional area of a saturated hydrocarbon chain,[22] and so they reflect the small size of the diazo ketone head group.

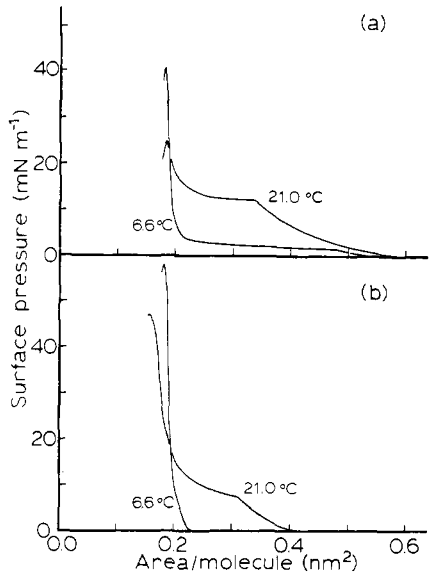


Figure 2. Surface pressure–area diagrams of monolayers of 1-diazo-2-oxopentadecane on water (a) without irradiation and (b) after 60 s of 254-nm irradiation at 0.65 nm^2/molecule.

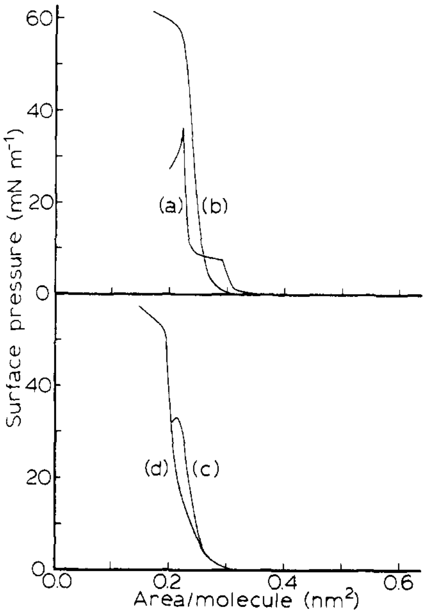


Figure 3. Surface pressure–area diagrams of monolayers of 1-(4-(octadecyloxy)phenyl)-2-diazo-1-oxoethane (**2**) and 4-(octadecyloxy)benzoyl azide (**1**) on water: (a) **2** without irradiation, 37.6 °C; (b) **2** after 60 s of 254-nm irradiation, 37.6 °C; (c) **1** without irradiation, 16.0 °C; (d) **1** after 60 s of 254-nm irradiation, 16.0 °C.

As expected, the temperature above which the starting diazo ketone forms expanded phases increases with increasing chain length. 1-Diazo-2-oxononadecane forms expanded phases above 39.0 °C, whereas the photoproduct monolayer shows only solid-analogue films up to our maximum experimental temperature of 45 °C. The C_{21} and C_{29} diazo ketones and their irradiation products give only solid-analogue monolayers below 45 °C.

Figure 2 also shows that the collapse pressure of the monolayer increases on irradiation. This behavior is displayed by every compound except the diazo ketone derived from oleic acid. Even in systems where no phase transition is produced by irradiation, the progress of the photoreaction can still be followed by observing the change in collapse pressure. Only when the alkyl chain is very long, as in the C_{29} diazo ketone, do the surface pressure–area curves of reactant and product monolayers become almost identical.

Figure 3 compares surface spreading behavior of a long-chain benzoyl azide **1** and a diazo ketone **2** of similar structure. Al-

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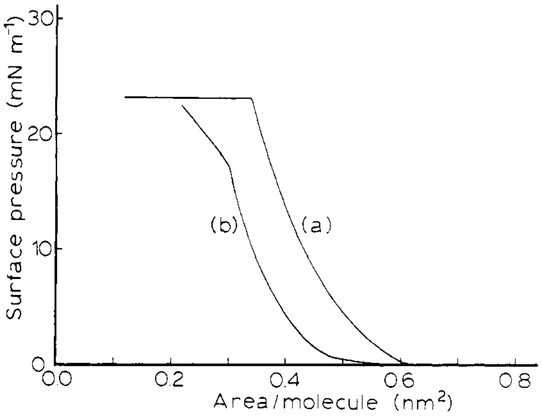


Figure 4. Surface pressure–area diagrams of monolayers of *cis*-1-diazo-2-oxo-10-nonadecene on water at 19.4 °C: (a) before irradiation and (b) after 90 s of 254-nm irradiation.

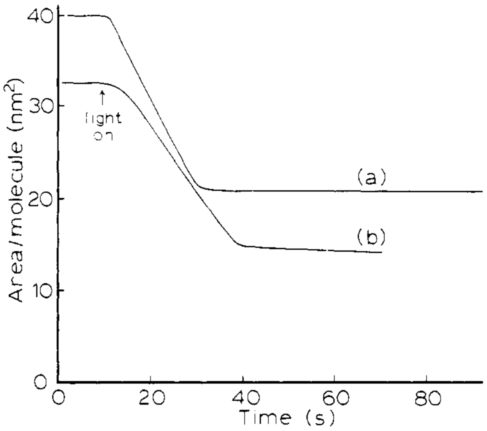


Figure 5. Variation of surface area of monolayers of diazo ketones on water during irradiation at constant pressure *P*: (a) 1-diazo-2-oxopentadecane at 11.9 °C, P = 5 mN m^{-1}, and (b) *cis*-1-diazo-2-oxo-10-nonadecene at 4.3 °C, P = 25 mN m^{-1}.

though the diazo and azide groups are of similar size, they have slightly different polarity, so that the diazo compound shows a well-defined expanded phase above 34 °C, whereas monolayers of the azide are unstable at this temperature. Both compounds react on irradiation to give solid-analogue monolayers having high collapse pressure.

Figure 4 illustrates the totally different spreading behavior resulting from the incorporation of a cis double bond into the alkyl chain of a diazo ketone. The more expanded packing of the unsaturated chains is reflected in the formation of liquid-analogue phases with inflection points at large surface areas, around 0.35 nm^2/molecule. Unlike all the other compounds investigated in this study, irradiated monolayers of *cis*-1-diazo-2-oxo-10-nonadecane show considerably lower collapse pressures than the starting films.

Collapse of a Monolayer by a Photochemical Reaction. When a monolayer of a photosensitive compound is irradiated at a constant applied pressure, the surface area can change remarkably. Figure 5 shows the change in surface area when monolayers of the C_{15} diazo ketone are irradiated at a constant pressure of 5 mN m^{-1}. The surface area decreases over 30 s from 0.40 to 0.22 nm^2/molecule as the expanded phase of the starting material disappears.

Even more pronounced effects are shown by monolayers of the cis-unsaturated diazo ketone (Figure 5). On irradiation at an applied pressure of 25 mN m^{-1} the surface area drops from 0.33 to 0.14 nm^2/molecule, well below the collapse area of the product monolayer. The partial collapse of the film arises because 25 mN m^{-1} lies below the collapse pressure of the starting monolayer but above that of the photoproduct.

Destruction of a Monolayer by a Photochemical Reaction. Figure 6 shows the change in spreading behavior produced by irradiation of monolayers of the C_{15} diazo ketone on 0.01 M aqueous NaOH. Only a small fraction of the photoproducts remain on the surface; the rest dissolves in the subphase, presumably as the anion of the carboxylic acid. The rate of dissolution of the irradiated film is slower at 6 °C than at 20 °C, but the steady state is still reached within 20 min. This effect is a consequence of the comparatively high solubility of the anion of pentadecanoic acid in water and is not manifested by diazo ketones having longer chains. This system illustrates the destabilization of a monolayer by a photochemical reaction.

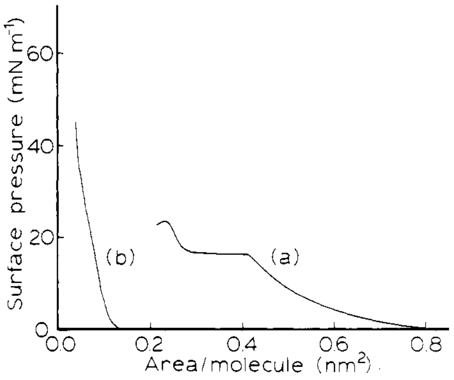


Figure 6. Surface pressure–area curves of 1-diazo-2-oxopentadecane on 0.01 M NaOH at 22 °C: (a) without irradiation and (b) irradiated 2 min at 0.65 nm^2/molecule and compressed after 20 min in darkness.

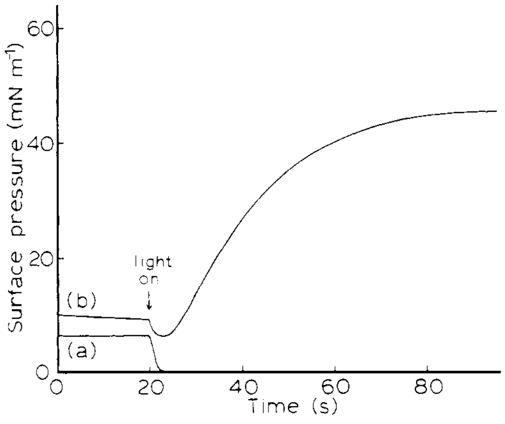


Figure 7. Variation of surface pressure with time during UV irradiation of monolayers of **2** at constant area *A* at 37.6 °C: (a) A = 0.28 nm^2/molecule (expanded phase) and (b) A = 0.21 nm^2/molecule (closest-packed phase).

Kinetics of Photoreactions in Monolayers. The rates of photoreactions in monolayers were obtained from measurements of the change in surface pressure with time at constant surface area. In principle the same information could be obtained from measurements of change in area at constant surface pressure, but in several cases the reactions were too fast to allow the servo unit of the film balance to adjust the surface area quickly enough.

It is conceivable that the surface pressure changes could lag behind the photoreaction, or even that the observed changes in surface pressure could correspond to only partial reaction of the monolayer. Two experiments were used to test for these possibilities. When the UV lamp was switched off in the middle of a photoreaction, the surface pressure stopped changing immediately. Second, monolayers were removed after different reaction times, and the extent of reaction was determined by IR spectroscopy. It was found that the diazo ketone bands disappeared completely at the same time the surface pressure reached its final value. These results show that the surface pressure responds sensitively to the changing composition of the monolayer on irradiation.

Figure 7 illustrates typical kinetic curves for monolayers of the aromatic diazo ketone **2**. The rate of change of the surface pressure is much greater when the film is irradiated in its expanded phase than when it is irradiated in the closest-packed state at 0.21

Table II. Times *t* for 50% Change of Surface Pressure during Irradiation of Monolayers at Constant Surface Area *A*

compound	*A*, nm²/ molecule	*T*, °C	*t*, s
1-diazo-2-oxopentadecane	0.40	6.6	3
1-diazo-2-oxopentadecane	0.18	6.6	33
1-diazo-2-oxononadecane	0.18	29.0	23
1-diazo-2-oxoheneicosane	0.19	29.2	17
dioctadecyl 2-diazopropanedioate	0.38	31.2	28
cis-1-diazo-2-oxo-10-nonadecene	0.42	11.6	9
azido ketone **1**	0.19	6.6	4
azido ketone **1**	0.19	21.2	3
diazo ketone **2**	0.28	37.6	1
diazo ketone **2**	0.21	37.6	21

nm²/molecule. This probably arises because the expanded phase disappears before the photoreaction is complete, rather than actually representing the influence of chain packing on the rate of the photoreaction.

Table II lists values of the irradiation times corresponding to 50% change in the surface pressure for monolayers of the various surface-active compounds. All of the photoreactions are rapid, proceeding to completion in under 90 s. High extinction coefficients at the exciting wavelength are necessary for rapid reaction. This is illustrated by studies of the photochemistry of the compound octadecanoyl azide in monolayers.[16] Because the aliphatic azido ketone has an extinction coefficient of only 300 M^{-1} cm^{-1} at 254 nm, its photoreactions were much slower, with typical half-reaction times of 20 min. As shown by the results for the long-chain azido ketone **1** in Table II, the rate of the photoreaction is only slightly affected by temperature. Several of the compounds showed very large changes in surface pressure on irradiation. For example, the surface pressure of monolayers of **1** jumps from 8 to 34 mN m^{-1}, an increase of over 300%, on irradiation at surface areas just above the collapse area of the starting compound.

Conclusions

The small size and comparatively simple photochemistry of the diazo ketone, diazo ester, and azide chromophores make long-chain compounds containing such hydrophilic groups well-suited for study in monolayers. Although the photoreactions are straightforward, the changes in head-group polarity produced by elimination of nitrogen and addition of water cause a wide variety of pronounced alterations in the behavior of these monolayers. Irradiation of monolayers of some compounds, such as 1-diazo-2-oxoheneicosane and dioctadecyl 2-diazopropanedioate, leads only to changes in monolayer compressibility and collapse pressure, without changing the monolayer structure. More pronounced changes are shown by monolayers of 1-diazo-2-oxononadecane and the aromatic diazo ketone **2**, which undergo phase transitions on irradiation. By irradiating monolayers of *cis*-1-diazo-2-oxo-10-nonadecane at high applied pressure, it is possible to push the monolayer off the water surface. Finally, irradiation of 1-diazo-2-oxopentadecane monolayers on an alkaline subphase leads to disappearance of the monolayers because the photolysis products are water soluble.

Acknowledgment. D. A. Holden thanks the Alexander von Humboldt-Stiftung for the award of a research fellowship (1981–1982). Thanks are also extended to Margret Deptolla for assistance with the synthesis of a number of the long-chain compounds.

Registry No. **1**, 90670-26-1; **2**, 90670-25-0; **3** (R = heptadecyl), 75240-80-1; 1-dizao-2-oxononadecane, 79196-27-3; 1-diazo-2-oxopentadecane, 90670-23-8; 1-diazo-2-oxoheneicosane, 80797-59-7; 1-diazo-2-oxononacosane, 90670-24-9; dioctadecyl 2-diazopropanedioate, 90670-27-2; *cis*-1-diazo-2-oxo-10-nonadecene, 90670-28-3; nonadecanoic acid, 646-30-0; 2-hydroxypropanedioic acid dioctadecyl ester, 90670-29-4; octadecanoyl chloride, 112-76-5; 4-(octadecyloxy)benzoyl chloride, 56800-40-9; dioctadecyl propanedioate, 16832-80-7; 4-octadecyloxybenzoic acid, 15872-50-1.

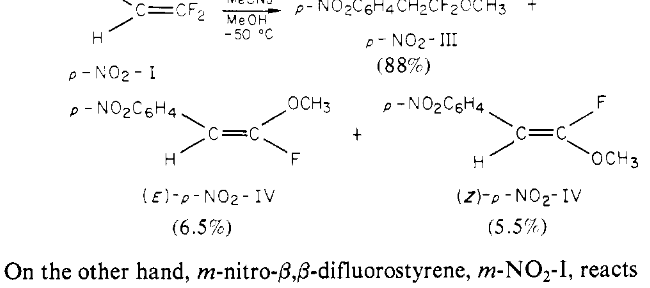
Proton-Transfer Reactions. 5.[1] An Observed Primary Kinetic Isotope Effect That Increases with Increasing Temperature

Heinz F. Koch* and Andrew S. Koch

Contribution from the Department of Chemistry, Ithaca College, Ithaca, New York 14850. *Received July 1, 1983*

Abstract: Reactions of $XC_6H_4CH{=}CF_2$ (I) with methanolic sodium methoxide result in formation of carbanions, $(XC_6H_4CHCF_2OMe)^-$ (II), that partition to yield $XC_6H_4CH_2CF_2OMe$ (III) and $XC_6H_4CH{=}CFOMe$ (IV). Product ratios for reactions in pure MeOD and MeOH are used to calculate the primary kinetic isotope effect (PKIE) associated with proton transfer from methanol to neutralize the carbanions. Compounds studied and their relative rates at 25 °C are *m*-CF_3-I (1.0), *m*-NO_2-I (7.7), *p*-CN-I (50), and *p*-NO_2-I (240). The calculated PKIE, k^H/k^D, for the neutralization reaction are as follows: *m*-CF_3-I, 1.28 (0 °C) and 1.40 (+50 °C); *m*-NO_2-I, 1.20 (−50 °C), 1.29 (0 °C), and 1.39 (+50 °C); *p*-CN-I, 1.33 (−70 °C), 1.36 (−50 °C), 1.69 (0 °C), and 2.11 (+50 °C); *p*-NO_2-I, 11.3 (−70 °C), 9.62 (−50 °C), 7.12 (0 °C), and 6.44 (+25 °C). The increase of PKIE with increasing temperature is discussed in terms of a multistep mechanism.

We recently reported significant differences for localized and delocalized carbanions that are neutralized by a competition between proton transfer from methanol, k_{add}^H, or by ejection of fluoride, k_{elim}^F.[2] For example, *p*-nitro-β,β-difluorostyrene, *p*-NO_2-I, reacts with methanolic sodium methoxide at −50 °C to yield 88% of a saturated ether, *p*-NO_2-III, and 12% of the isomeric vinyl ethers, (*E*)- and (*Z*)-*p*-NO_2-IV.



On the other hand, *m*-nitro-β,β-difluorostyrene, *m*-NO_2-I, reacts

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