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PHOTOCHEMISTRY OF REACTIVE SURFACE-ACTIVE COMPOUNDS IN ADSORBED MONOLAYERS

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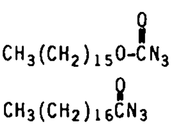
Abstract - The reactions of long-chain diazo ketones and azides in adsorbed monolayers on inorganic solids were investigated and compared with the corresponding behaviour in monolayers at the air-water interface. The isolated products indicate that reaction of photochemically generated intermediates occurs both with co-adsorbed water and with hydroxyl groups on the solid surface. In the case of 1-diazo-2-oxoheptadecane, for example, the products of these two reactions are heptadecanoic acid and a surface-grafted long-chain ester. The latter can be removed as methyl heptadecanoate by ester exchange using methanolic HCl. Pronounced differences were observed between alumina, silica gel and fumed silica as supports, and were attributed to differences in the amount of adsorbed H_2O and in the density of surface hydroxyl groups.

Recently there has been considerable interest in the photochemistry of compounds adsorbed on the polar surfaces of inorganic materials such as silica gel and alumina.[1-5] For the most part, however, such research is concerned with possible modification of the mechanisms or product distributions of photoreactions as a result of adsorption. Much less attention has been devoted to photoreactions between adsorbed molecules and functional groups on the underlying surface.

This publication describes the development of photochemical reactions of adsorbed monolayers as a technique for modifying solid surfaces. This surface grafting technique differs from the well-established silylation of hydrophilic surfaces[6-9] in that it is a two-step procedure, as illustrated conceptually in Fig. 1. In the first step chemisorption of a long-chain compound stable to hydrolysis occurs from hydrocarbon solution to give monolayer coverage of the surface.[10] In the second step the grafting reaction is carried out by UV irradiation or heating.

Many classes of photosensitive compounds have been investigated in such organized systems as liposomes or monolayers at the air-water interface. These include diazonium salts,[11] azobenzene derivatives[12], azenes[13], azides and diazoketones[14-16]. For the present study of photochemistry in monolayers at the solid-liquid interface, the long-chain azides and diazoketones shown in Chart I were chosen, both for their ease of synthesis and because they have compact hydrophilic groups similar in polarity to the carboxylic acid functional group.



$CH_3(CH_2)_n\overset{O}{\overset{\|}{C}}CH{=}N_2$ n = 14, 16

$CH_3(CH_2)_{15}O{-}\overset{O}{\overset{\|}{C}}N_3$

$CH_3(CH_2)_{16}\overset{O}{\overset{\|}{C}}N_3$

Chart I

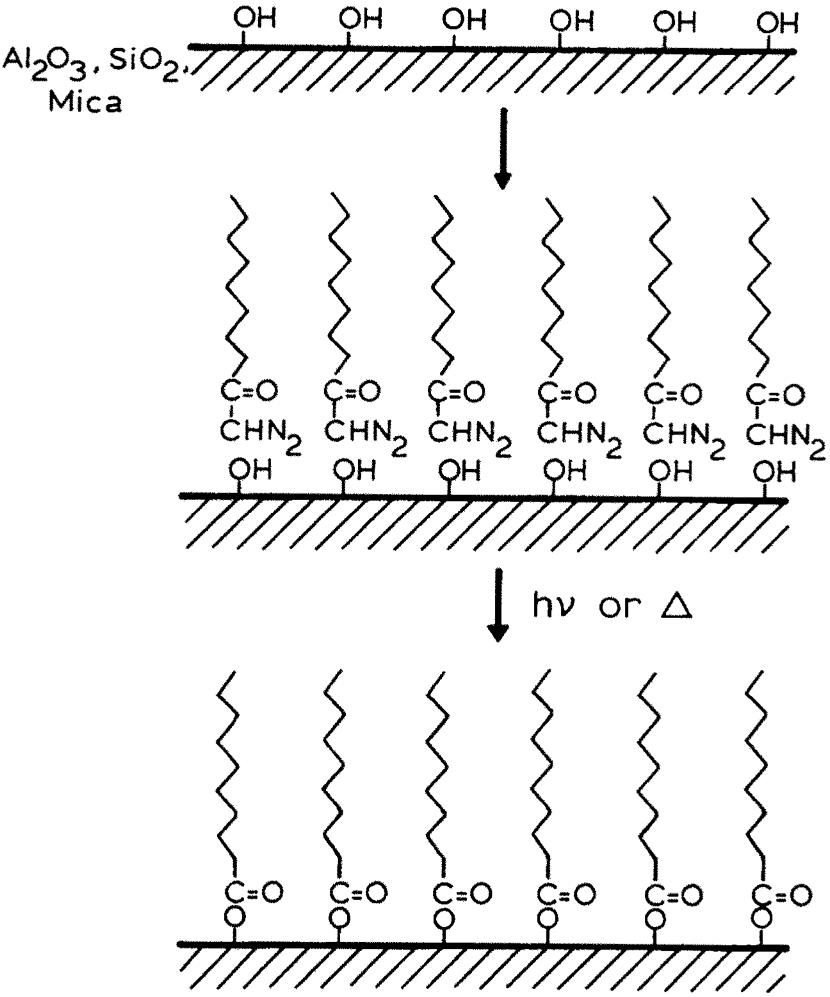


Figure 1: Grafting of a long-chain diazoketone on dry alumina by chemisorption and photochemical reaction

Inorganic solids treated by this photochemical grafting procedure are strongly hydrophobic. While the resistance to solvolysis of the chemical bond with the surface is rather low in some cases, there may be a role for this photochemical grafting technique in such areas as the production of coatings and composite materials.

RESULTS AND DISCUSSION

Figure 2 compares the surface pressure - surface area behaviour of monolayers of 1-diazo-2-oxoheptadecane and 1-diazo-2-oxononadecane on pure water before and after 254 nm irradiation. Both the starting material and the photoproduct mixture give stable monolayers at the air-water

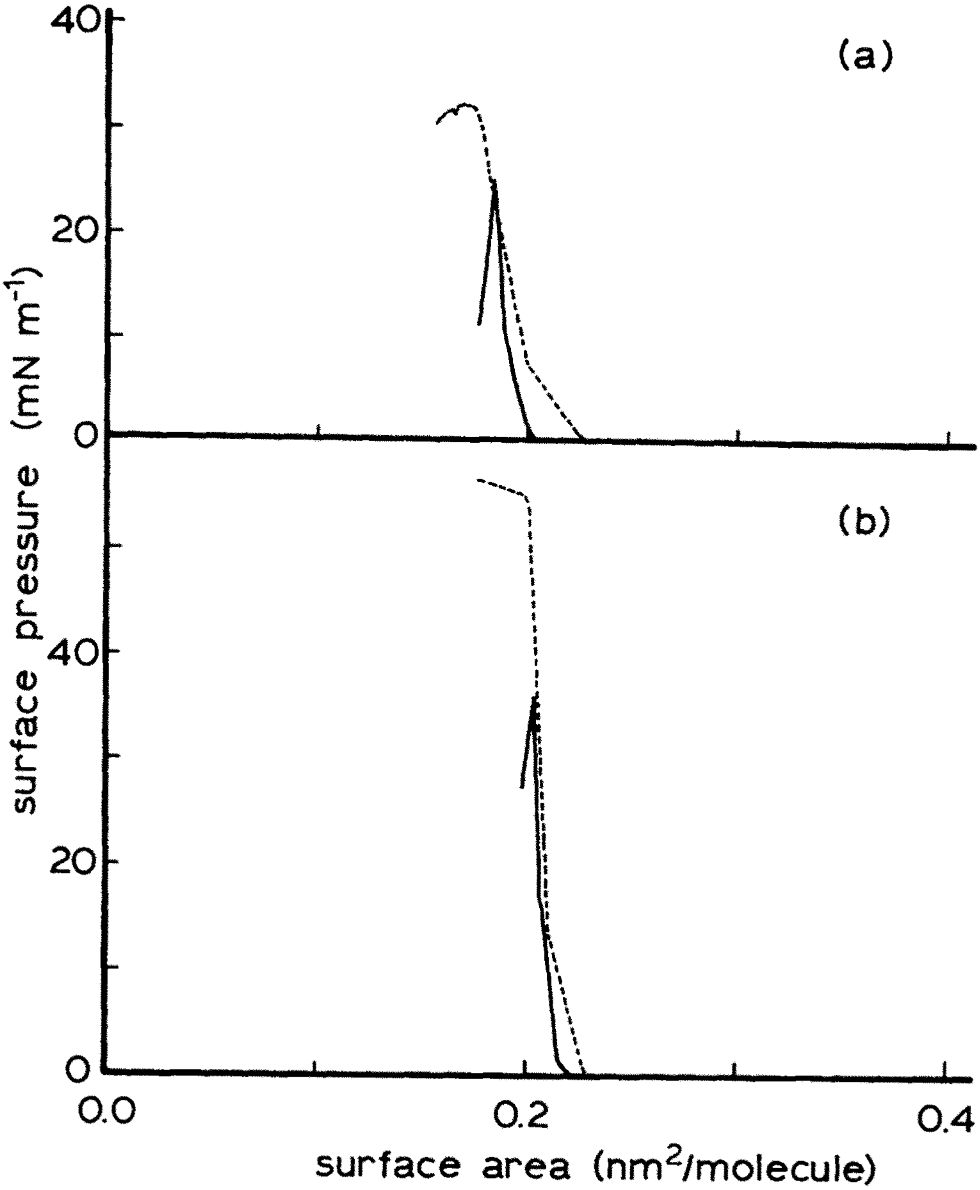


Figure 2: Surface pressure - surface area diagrams of monolayers on water: a) (——) 1-diazo-2-oxoheptadecane, 12.1°C; (---) after 5 minutes 254 nm irradiation; b) (——) 1-diazo-2-oxononadecane, 20.8°C; (----) after 90 s 254 nm irradiation.

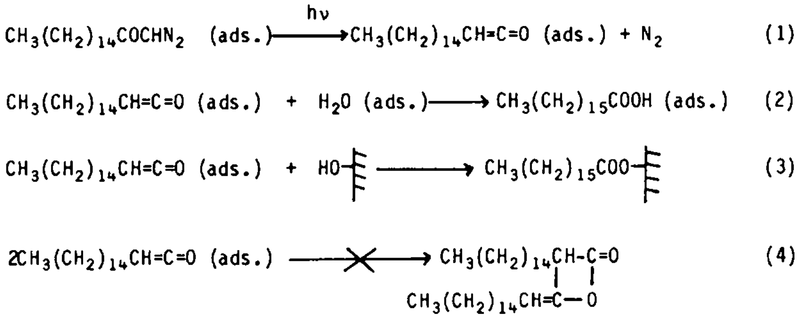
interface, and form solid-analogue phases with molecular areas of 0.19 to 0.20 nm^2/molecule, values characteristic of the cross-section of hydrocarbon chains. It was shown similarly that all other compounds used in this study were strongly surface-active and that the products of reaction in monolayers were also surface-active.

Photochemistry of Diazoketones at the Solid-Liquid Interface

When a hexane solution of 1-diazo-2-oxoheptadecane is shaken with neutral alumina, the solution becomes colourless immediately and the alumina turns very pale yellow. Adsorption of the long-chain compound is quantitative, as indicated by the absence of starting material in the decanted solvent. That no chemical grafting has taken place prior to irradiation is shown by the ability of more polar solvents such as $CHCl_3$ to extract the unreacted starting material.

After 2-4 hours of 254 nm irradiation the reaction of the adsorbed diazoketone is complete, as indicated by the absence of starting material in subsequent elution fractions. Elution with $CHCl_3$ or ethyl acetate gives variable amounts of heptadecanoic acid. Extraction with methanol fails to remove additional products, but elution with methanolic HCl affords partial recovery of product as methyl heptadecanoate.

Equations 1 to 4 describe the chemistry taking place in monolayers of diazoketones on alumina.



$$CH_3(CH_2)_{14}COCHN_2\ (ads.) \xrightarrow{h\nu} CH_3(CH_2)_{14}CH{=}C{=}O\ (ads.) + N_2 \quad (1)$$

$$CH_3(CH_2)_{14}CH{=}C{=}O\ (ads.) + H_2O\ (ads.) \longrightarrow CH_3(CH_2)_{15}COOH\ (ads.) \quad (2)$$

$$CH_3(CH_2)_{14}CH{=}C{=}O\ (ads.) + HO- \longrightarrow CH_3(CH_2)_{15}COO- \quad (3)$$

$$2CH_3(CH_2)_{14}CH{=}C{=}O\ (ads.) \xrightarrow{\times} \begin{matrix} CH_3(CH_2)_{14}CH-C{=}O \\ | \quad\ \ | \\ CH_3(CH_2)_{14}CH{=}C-O \end{matrix} \quad (4)$$

Scheme 1

As was the case for the analogous photoreaction in monolayers on water,[16] a ketene intermediate is generated photochemically at the interface (eq. 1). This reacts either with co-adsorbed H_2O to give a long-chain carboxylic acid, or with surface OH groups to give a chemically grafted ester. A significant difference between the photoreactions in monolayers on Al_2O_3 and on water is the absence of dimerization products of the ketene (eq. 4).[16] The resulting β-lactones are easily recognized by an intense IR C=O band around 1825 cm^{-1}, a region where few carbonyl compounds absorb. This difference may reflect reduced translational freedom of compounds in monolayers on the solid surfaces.

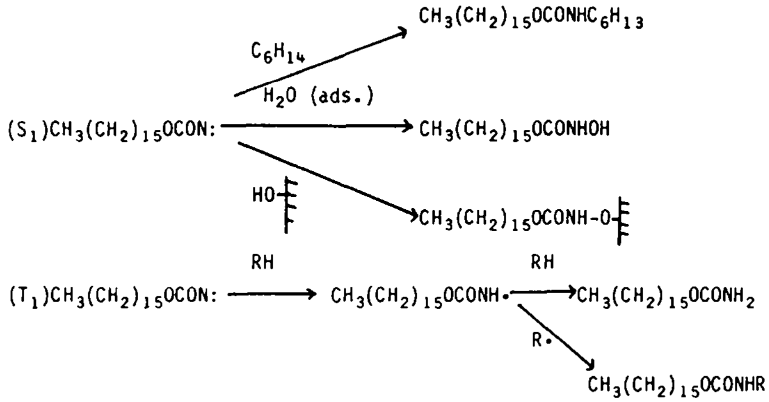
The eluted carboxylic acid is not the hydrolysis product of a species which was grafted on the surface, since it is eluted by the same aprotic solvents which remove adsorbed palmitic and stearic acids. Further evidence that it comes from the reaction between adsorbed ketene and a monolayer of adsorbed water comes from its highly variable yield. In reactions on alumina, the yield of carboxylic acid is low for fresh or dried Al_2O_3, and increases with the extent of prior exposure to atmospheric moisture. In contrast nonadecanoic acid is the only isolated product from the reaction of the C_{19} diazoketone in monolayers on silica gel having a higher surface water content.

While the long-chain carboxylic acids are products which are adsorbed but not chemically bonded to the surface, methyl esters correspond to hydrolysis of a precursor which was indeed bonded to the surface. If this were not the case, methyl heptadecanoate would have been eluted by even weakly polar solvents such as hexane/CH_2Cl_2 mixtures, instead of by acidic methanol.

Photochemical Grafting of Azides on Solid Surfaces

Hexadecyl azidoformate undergoes photoreaction to completion in adsorbed monolayers on both alumina and silica gel. The sole isolated product from the reaction on alumina is 1-hexadecanol, which is eluted by CH_2Cl_2 and ethyl acetate in up to 90% yield. In contrast the reaction on silica gel affords no long-chain alcohol, only traces of O-hexadecyl carbamate, eluted by CH_2Cl_2, together with a mixture of urethanes formed by C-H insertion of the photochemically generated nitrene shown in the proposed Scheme 2:[17,18]

$$CH_3(CH_2)_{15}OCON_3 \xrightarrow{h\nu} CH_3(CH_2)_{15}OCON: \ + \ N_2 \qquad (5)$$



(6)

(7)

(8)

(9)

Scheme 2

The N-hydroxy carbamate, which would be formed by the reaction of singlet nitrene with adsorbed H_2O (eq. 7), was not isolated from the reaction on either substrate. 1-Hexadecanol may arise from hydrolysis by adsorbed H_2O of both this product and the surface-grafted species formed in eq. 8. An alternative route is via fragmentation of the triplet nitrene (eq. 10),

$$CH_3(CH_2)_{15}OCON: \longrightarrow CH_3(CH_2)_{15}O\cdot \ + \ \cdot NCO \xrightarrow{RH} CH_3(CH_2)_{15}OH \qquad (10)$$

but this is normally only observed in the gas phase because of the high reactivity of both singlet and triplet nitrenes in condensed media.[17,18] The marked difference in the yield of 1-hexadecanol on neutral alumina and silica gel may reflect the relative basicities of the two surfaces.

The sole isolated product from the photoreaction of octadecanoyl azide adsorbed on silica gel is N,N'-diheptadecyl urea in less than 5% yield. No products could be isolated from the same reaction on alumina, until elution with CH_2Cl_2/MeOH containing 2% concentrated NH_4OH gave less than a 5% yield of stearic acid. Formation of the urea derivative is evidence for the Curtius reaction (Scheme 3), which also requires the involvement of co-adsorbed H_2O.

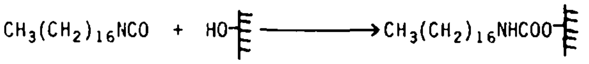
$$CH_3(CH_2)_{16}CON_3 \xrightarrow[\text{or } \Delta]{h\nu} CH_3(CH_2)_{16}NCO \ + \ N_2 \qquad (11)$$

$$CH_3(CH_2)_{16}NCO \ + \ H_2O\ (\text{ads.}) \longrightarrow CH_3(CH_2)_{16}NH_2 \ + \ CO_2 \qquad (12)$$

$$CH_3(CH_2)_{16}NH_2 \ + \ CH_3(CH_2)_{16}NCO \longrightarrow CH_3(CH_2)_{16}NHCONH(CH_2)_{16}CH_3 \qquad (13)$$

Scheme 3

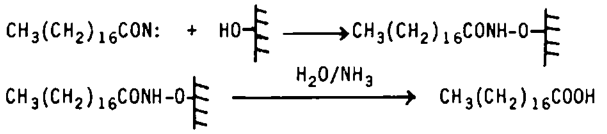
The reaction of the long-chain amine with isocyanate is apparently able to compete with the reaction between adsorbed water and isocyanate, as no heptadecylamine was isolated. Because of the durability of the chemical bond with the surface, no products could be removed which would establish the nature of the grafting reaction, but a likely reaction involves urethane formation from the isocyanate, as shown in eq. 14.


(14)

$$CH_3(CH_2)_{16}NCO \ + \ HO- \longrightarrow CH_3(CH_2)_{16}NHCOO-$$

The formation of stearic acid under hydrolytic conditions is evidence for the intermediacy of acyl nitrene (eq. 15-17), a species known to be generated together with isocyanates in the photolysis of acyl azides in homogeneous solution.[17]

$$CH_3(CH_2)_{16}CON_3 \xrightarrow{h\nu} CH_3(CH_2)_{16}CON: \ + \ N_2 \qquad (15)$$



$$CH_3(CH_2)_{16}CON: + HO- \longrightarrow CH_3(CH_2)_{16}CONH-O- \quad (16)$$

$$CH_3(CH_2)_{16}CONH-O- \xrightarrow{H_2O/NH_3} CH_3(CH_2)_{16}COOH \quad (17)$$

Even at 35°C there is an appreciable thermal component to the decomposition of acyl azides, and it is possible to achieve complete thermal decomposition of adsorbed azide in refluxing cyclohexane. Again the isolated products include N,N'-heptadecyl urea, but the thermal reaction also yields substantial 1-heptadecyl isocyanate, which undergoes partial desorption at the higher reaction temperature and is eluted by hexane. Photochemical grafting thus offers an advantage over thermal grafting because it is carried out at temperatures low enough to minimize desorption of either the starting material or its primary photolysis product. Similarly the two-stage adsorption-photolysis procedure differs from modifications which could be carried out by treating a surface with a hexane solution of a long-chain ketene or isocyanate, because the strong adsorption in the former procedure means that smaller amounts of reactive surface-active compound are required.

Comparison of Substrates

It must be emphasized that the products isolated by elution as described in the preceding sections generally represent only a small fraction of the total products, and that the bulk of the reaction products could not be eluted by any non-reactive solvent. With the exception of hexadecyl azidoformate on alumina, treatment of alumina or silica gel by photochemical reactions of long-chain compounds resulted in high yields of grafting, as shown by the results of Table 1.

Table 1. Degree of Grafting of Long-chain Compounds Adsorbed on Inorganic Solids

Compound[a]	% grafting on[b] Al_2O_3	silica gel	fumed silica
1-diazo-2-oxononadecane	81	93	48
hexadecyl azidoformate	11	93	54
octadecanoyl azide	95	96	--

[a] At 1% by weight

[b] Defined as % not eluted by solvents increasing in polarity to 1:1 $CHCl_3$/methanol

The extent of grafting to fumed silica was considerably lower than to silica gel, but was increased by treatment with 5% aqueous HCl, followed by prolonged drying. This result is attributed to the lower density of OH groups on the surface of fumed silica, and indicates that hydrophobization of the surface is most successful if the surface is initially strongly polar.

EXPERIMENTAL SECTION

Materials

The syntheses of 1-diazo-2-oxononadecane and hexadecyl azidoformate are described in earlier publications.[15,16] 1-Diazo-2-oxoheptadecane was prepared following the general procedure[16] and was recrystallized several times from CH_2Cl_2/hexanes at -20°C. The compound forms large yellow flakes, m.p. 59.5-60°C; IR(Nujol): 3080 cm^{-1} (unsaturated C-H stretch), 2122, 2100 (C=N=N), 1620 (conjugated C=O); ^1H NMR ($CDCl_3$): δ 5.19 (s, 1H), 2.33 (t, 2H), 1.26 (unresolved m, 26 H), 0.88 (t, 3H); UV (hexane) λ_{max} 383 nm (ϵ 13.2 M^{-1} cm^{-1}), 247 (13800). Octadecanoyl azide was prepared by the reaction of stearoyl chloride with excess HN_3 in dry CH_2Cl_2 at 0°C in the presence of 1 equiv. of pyridine. The product was recrystallized from 1/2 CH_2Cl_2/hexanes between 20°C and -78°C and had m.p. 41-43°C with decomposition. IR (Nujol): 2137 cm^{-1} (N_3), 1712 cm^{-1} (C=O). The isocyanate band at 2271 cm^{-1} was almost absent.

Monolayer Studies

Monolayers at the air-water interface were characterized using a Langmuir balance similar to the balance described by Albrecht.[20] Surface pressure was measured by the Wilhelmy hanging plate technique, with 1 cm x 1.5 cm strips of filter paper as the wettable material. A reference hanging plate immersed in the pure water side of the trough allowed correction for changes in the water level. Other than this filter paper the only material in contact with the sub-phase was solid Teflon. The entire balance was under glass to minimize contamination from air-borne impurities, and was isolated from vibration by resting on an air-suspension table (Technical

Manufacturing Corp.). Movement of the barrier, measurement of surface pressure and temperature, as well as data analysis and plotting were controlled by a Hewlett-Packard 87 XM computer interfaced to the balance through a Hewlett-Packard 3421 A data acquisition unit. Temperature control of the sub-phase was provided by a Haake refrigerated constant temperature bath which circulated water through the base plate of the balance. Irradiation of monolayers on water was carried out using a bank of 6 10 W low-pressure Hg lamps mounted in the cover of the Langmuir trough. For monolayer studies water was purified to a conductivity of 18 MOhm-cm by using a Milli-Q filtration system. Compounds were spread from 1 mg/mL solutions in chloroform (J.T. Baker Photrex grade) using a microsyringe with a Chaney adapter.

Photochemical Reactions of Monolayers Adsorbed on Solid Surfaces

All irradiations were carried out in a horizontal quartz tube using a Rayonet RPR-100 photoreactor turned on its side. The reaction temperature was 35°C. Samples were tumbled continuously during irradiation. In a typical experiment 0.1 g of 1-diazo-2-oxoheptadecane in 15 ml hexane (J.T. Baker Photrex grade) was shaken with 10 g neutral alumina (J.T. Baker, 80-200 mesh) for 30 seconds. The hexane was then decanted and replaced with fresh solvent and the slurry was irradiated under nitrogen at 254 nm for 2 hours. In an alternative procedure the coated powder was filtered by suction and dried in air, and the irradiation was carried out without the use of a solvent. In other reactions silica gel (J.T. Baker, 70-230 mesh) and fumed silica (Sigma, particle size 0.014 μm) were used without further drying.

Thermal Reactions of Adsorbed Monolayers

Thermal grafting of long-chain azides was carried out for comparison with photochemical grafting. In a typical experiment 15 g of silica gel was mixed with a solution of 0.15 g octadecanoyl azide in 50 ml of hexane and the suspension was stirred and refluxed for 3 h.

Analysis of Products

Identification of products and measurement of the extent of grafting were carried out by using the surface-treated solids as packings for column chromatography. Elution with increasingly polar solvents was carried out under 10 psi N_2 pressure. A typical elution sequence used hexane, hexane/CH_2Cl_2 mixtures, CH_2Cl_2, CH_2Cl_2/EtOAc mixtures, EtOAc, EtOAc/MeOH mixtures, MeOH and finally methanol containing 1% aqueous HCl to solvolyze chemically bound species. In other runs, mixtures of ethanol and diethylamine or aqueous ammonia were used in the final elution step. Reaction products obtained by elution with alcohols were separated from suspended inorganic particles by subsequent extraction into CH_2Cl_2. In some cases mixtures of eluted products were separated into hexane-soluble and hexane insoluble fractions and further purified by recrystallization. Major products were identified by IR and ^1H NMR spectroscopy by comparison with spectra of authentic compounds. Methyl heptadecanoate was obtained by the Ag^+-catalyzed decomposition of 1-diazo-2-oxoheptadecane in methanol. N,N'-diheptadecyl urea was prepared by the thermal Curtius reaction of octadecanoyl azide in 2:1 dioxane-water. N-heptadecyl O-ethyl carbamate was obtained by decomposition of octadecanoyl azide in ethanol. Additional compounds were available from previous studies.[15]

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