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Structure and reactions in novel organic monolayers

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Case Western Reserve University, 1990
STRUCTURE AND REACTIONS IN NOVEL ORGANIC MONOLAYERS

by

JOHN GREGORY SKABARDONIS

Submitted in partial fulfillment of the requirements for the Degree of Doctor of Philosophy

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August 1990
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(Chairman)

Date 5/27/90

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Structure and Reactions in Novel Organic Monolayers

Abstract

by

John Gregory Skabardonis

1-Diazo-2-oxoalkanes

Long chain molecules possessing a diazomethyl ketone functionality have been used to form Langmuir films which were subsequently photolyzed with varying amounts of area available to the individual molecules. Photolysis of a diazomethyl ketone can give rise to a variety of carbene and/or ketene derived products. The properties of the films arising from these photolyses were compared to those formed from independently prepared long chain carboxylic acids, α-hydroxy ketones, and their mixtures. Creep tests and π/α isotherms of the photolyzed films indicated that very stable films were formed. Viscosity measurements were done on the films formed from the photolyses of diazomethyl ketone films. Canal viscosimeters of varying widths were used and these experiments clearly showed that film viscosity depends on the amount of area available to the molecules during the photolysis. The films displayed viscosities that were much higher than those of the possible carboxylic acid or α-hydroxy ketone products.
The canal viscosimetry method has previously been used to measure the surface shear viscosity of monolayers. In those instances however, the viscosity at a single surface pressure was measured. In the modification of the method that we have used, the surface shear viscosity corresponding to an entire range of surface pressures can be calculated in a single experiment.

[22.3.3]Propellanes

[22.3.3]propellanes containing ketone and/or hydroxyl functionalities were used to form Langmuir films whose properties were studied. A model has been proposed to allow an understanding of how these unusually shaped molecules orient themselves at the air/water interface and how they efficiently fill space in a monolayer.

Tritium has been used to label a [22.3.3]propellane ketol, thus permitting the monitoring of the ratio of products formed when a Langmuir film of the material undergoes reduction with sodium borohydride. The ratio of products formed when a propellane film was reduced with varying amounts of area available to the molecules was compared to the ratios obtained when the material was reduced in the presence of micelles and in the bulk state. It was shown that the ratio of products formed from the reduction in the monolayer more closely resembles that obtained from the reduction in the bulk rather than that from the reduction in the presence of micelles.
Dedication

This work is dedicated to Dina, my loving and caring wife. Without her support, patience and understanding it would have been much harder to complete it. For my family's faith in my abilities and their extensive support, I also dedicate this work to them.
Acknowledgements

I wish to acknowledge the guidance and support of Prof. Chaim N. Sukenik. This research was conducted at the fringes of the domain of Physical Organic chemistry, in an area in which neither of us had much experience. The learning process has been frustrating as well as fascinating.

Prof. Jay A. Mann has taught me the basic theory as well as the nuances involved in Langmuir film research. His patience and understanding are greatly appreciated. He has also written the software for the surface shear viscosity determination and has spent many hours tutoring me in its use. In conjunction with Professors Scott E. Rickert and Jerome B. Lando he has allowed me to use the Polymer Microdevice Laboratory (PML) and all the equipment necessary for Langmuir film formation and manipulation.

Professor Marc S. Berridge helped with the logistics of the tritium labelling experiment, as well as with all the training involved to conduct it safely. He also allowed use of the capillary column Gas Chromatograph (GC) in his laboratory for the analysis of recovered Langmuir films. Dr. Jerry Reed-Mundell helped to obtain the Cyclic Voltammogram (CV) data. Dr. S. Harik M.D. allowed use of the High Pressure Liquid Chromatograph equipped with Electrochemical Detector (LCEC) in his laboratory.
Drs. Casper Chiang, Joel Shutt and Rashmi Sudiwala provided me with the basics of the Lauda film balance operation, film formation and manipulation. Steve Walsh and Andy Dewa helped to understand and repair the mechanical and electrical intricacies of the film forming equipment.

Special thanks are directed to Dr. Anand Natrajian, who synthesized all the propellanes, Dr. John D. Hays for his help with the CHEMGRAF and CHEMLAB molecular modelling software, and Lou Martino, Andy Tanos and Adrian Valeriu who helped with instrumentation. I want to thank all my friends and colleagues and the faculty and staff of the Chemistry Department for making my stay at C.W.R.U. an enjoyable and memorable experience.

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<tr>
<td>a,a diol</td>
<td>[22.3.3]Propellane anti, anti diol</td>
</tr>
<tr>
<td>ATR</td>
<td>Attenuated Total Reflectance</td>
</tr>
<tr>
<td>C17 acid</td>
<td>Heptadecanoic acid</td>
</tr>
<tr>
<td>C18 acid</td>
<td>Nonadecanoic acid</td>
</tr>
<tr>
<td>CIMS</td>
<td>Chemical Ionization Mass Spectroscopy</td>
</tr>
<tr>
<td>CTABr</td>
<td>Cetyltrimethylammonium bromide</td>
</tr>
<tr>
<td>DDABr</td>
<td>Didodecyldimethylammonium bromide</td>
</tr>
<tr>
<td>DOA</td>
<td>1-Diazo-2-oxoalkanes</td>
</tr>
<tr>
<td>DOH</td>
<td>1-Diazo-2-oxoheptadecane</td>
</tr>
<tr>
<td>DON</td>
<td>1-Diazo-2-oxononadecane</td>
</tr>
<tr>
<td>DOP</td>
<td>1-Diazo-2-oxopentadecane</td>
</tr>
<tr>
<td>FID</td>
<td>Flame Ionization Detector</td>
</tr>
<tr>
<td>FTIRRAS</td>
<td>Fourier Transform Infrared Reflection Absorption Spectroscopy</td>
</tr>
<tr>
<td>GC-IR</td>
<td>Gas Chromatographic analysis in tandem with Fourier Transform Infrared Spectroscopy</td>
</tr>
<tr>
<td>HK</td>
<td>α-Hydroxy ketone</td>
</tr>
<tr>
<td>LCEC</td>
<td>Liquid Chromatography utilizing an Electrochemical Detector</td>
</tr>
<tr>
<td>LVDT</td>
<td>Linearly Variable Differential Transformer</td>
</tr>
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<td>OHD</td>
<td>2-Oxoheptadecanol</td>
</tr>
<tr>
<td>OND</td>
<td>2-Oxononadecanol</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
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<tr>
<td>(\pi/A)</td>
<td>Pressure/Area</td>
</tr>
<tr>
<td>PML</td>
<td>Polymer Microdevice Laboratory</td>
</tr>
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<td>s,a diol</td>
<td>[22.3.3]Propellane syn, anti diol</td>
</tr>
<tr>
<td>s,s diol</td>
<td>[22.3.3]Propellane syn, syn diol</td>
</tr>
<tr>
<td>SFC</td>
<td>Supercritical Fluid Chromatography</td>
</tr>
<tr>
<td>TEAP</td>
<td>Tetraethylammonium perchlorate</td>
</tr>
<tr>
<td>TMABr</td>
<td>Tetramethylammonium bromide</td>
</tr>
<tr>
<td>TMAO</td>
<td>Trimethylamine oxide</td>
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Chapter I. Introduction

I.1. Background

The effects of oils on water surfaces have been observed since antiquity. The ancient civilizations that resided around the Mediterranean were aware of the fact that if oil was poured on rough seas, the waves would be calmed. Yet, it was not until the very beginning of the twentieth century that scientists tried to arrive at an explanation for the phenomenon. Rayleigh proposed that the oils formed thin films that were only one molecule thick giving rise to the term "monomolecular films". Hardy showed that oils with no polar functional groups did not spread like fatty acids. Then, in 1917, Langmuir wrote a landmark paper in which he demonstrated that in films of fatty acids each molecule occupies approx. 20 Å, regardless of the length of the molecule's polymethylene chain. He concluded that monolayers were being formed, in which the molecules were closely packed and the polar carboxyl groups were immersed in the water, while the long nonpolar chains were directed away from the water. To perform the measurements he constructed a type of trough where a movable barrier was used to manipulate a film on the water surface and a float attached to a balance measured surface forces as it was deflected by the film (this kind of set-up is now referred to as a Langmuir film balance). A few years later Harkins proposed a
theory for molecular orientation at surfaces. Working independently and due to his interest in the surface phenomena associated with ore separation, Langmuir proposed a similar theory at the same time. Langmuir also showed that films could be transferred onto solid supports by dipping the support vertically through the film covered interface and that the film's orientation varied depending on the surface tension (determined by the contact angle with water) of the support. Blodgett, one of Langmuir's co-workers, showed that by successively dipping and withdrawing a suitable substrate through the film, multilayers of the Langmuir films could be prepared. This is now referred to as the Langmuir-Blodgett process.

1.2. Monolayers: Langmuir Films and Adsorbed Films

A Langmuir film is formed by slowly dripping a dilute solution of an amphiphilic material onto a clean water surface and allowing the solvent to evaporate. The surface-active molecules are restricted to the interface, with their polar head-groups bound to the aqueous subphase and their hydrophobic tails assuming various orientations relative to the surface plane, depending upon the available area per molecule (Figure 1.2.1). It is possible to manipulate the orientation and degree of organization of molecules in a monolayer assembly and to directly control the approach of molecules to each other by variation of the surface area available
to the molecules. In a tightly packed monolayer the molecules are ordered as if in a two-dimensional crystal and if the monolayer is compressed any further, the film collapses. This high degree of order can be transferred to a solid substrate that is passed through the film (Langmuir-Blodgett method), thereby creating multilayers (Figure I.2.2). The fact that there is good filling of space in a closely packed monolayer should not, however, confuse us into assuming that it behaves as an inflexible solid. It has been shown that even multilayers of cadmium arachidate (which produce a
Figure I.2.2. Langmuir-Blodgett multilayer formation.
well packed film displaying a high collapse pressure) are fluid enough to allow diffusion of small molecules (naphthalene derivatives) through them without serious perturbations to their structure.\textsuperscript{3}

An alternate method of monolayer formation also exists, in which the amphiphilic material is dissolved in a non-polar solvent and it then adsorbs onto any surface that comes into contact with the solution. Although it was first reported by Bigelow\textsuperscript{10} in 1946, only recently has interest been expressed in the self-assembly method. In Bigelow's work the monolayers are physisorbed onto the substrate with no covalent bonds holding them to the surface. In a modification of this method the molecule's polar group is replaced by a trichlorosilyl functionality which, during the self-assembly process, forms a chemical bond with hydroxyl groups that may be present on the substrate and also crosslinks to its nearest neighboring molecules.\textsuperscript{11} After the film is formed, it can be subjected to chemical transformations which will modify the functionality that it presents to the environment.\textsuperscript{12}

Finally, some materials form monolayers when a small amount of an aqueous dispersion is allowed to evaporate on a polypropylene substrate.\textsuperscript{13} The films formed however do not exhibit the same order that is found in films formed through the Langmuir-Blodgett or self-assembly methods, as individual molecules are found to be rotated by 180° relative to each other. In general, this method
usually produces bilayers or multilayers,\textsuperscript{14} requiring molecules of a very specific conformation to give rise to monolayers and thus limiting its value.

I.3. Applications

Monolayers represent a very organized supramolecular assembly which exhibits a very high degree of ordering of its constituent molecules. The highly ordered nature of such ultra-thin monolayers and of multilayers makes them both interesting and useful. A recent review article\textsuperscript{15} provides an excellent overview of the various areas where monolayer applications can be expected to make the largest contributions. Possible applications in the area of thin film optics include nonlinear optical effects, second harmonic generation, as well as light guiding in Langmuir-Blodgett films.\textsuperscript{16} Thin films are already in the testing stages for utilization as selective sensors for gases and other environmental contaminants.\textsuperscript{17} Langmuir-Blodgett monolayers and multilayers are used as photoresists and as electron beam microlithography materials.\textsuperscript{14} In the area of lubrication, it was shown that the frictional wear resistance provided from only one monolayer on each of the rubbing surfaces was vastly superior to physisorbed lubricants of equivalent thickness.\textsuperscript{17} Finally, since monolayers bear a striking resemblance to biological membranes, it is hoped that they will
lead to a better understanding and utilization of protein and lipid films.

I.4. The Air/Water Interface

Throughout this discussion we will be referring to films formed on the water surface. There is however, no such thing as a free surface in nature. We are always dealing with the boundary region between two phases, an interface. Furthermore, the interface is not a sharp demarcation from one phase to the next, but rather it is a transition region between the two phases. The area immediately above the bulk water phase is air with a few water molecules interspersed inside it and the area immediately below the bulk air phase is water with a few air-component molecules mixed-in. The thickness of this transition region is not very large (a few molecular diameters at most) due to the very short range for the forces of attraction and repulsion between neutral molecules. The very fact that monolayers do in fact form at the air/water interface was used by Langmuir to propose that the transition region is very thin. If this were not the case, other types of molecular assemblies (than monolayers) would be formed. For simplicity however, the interface will be referred to as the water surface.
I.5. Surface Tension

Whenever working with water, its surface tension will play a major role in the phenomena observed. This is the force produced from unbalanced molecular attraction which tends to pull molecules into the interior of the liquid phase and therefore tends to minimize the surface area (the reason water drops are round). When studying a monolayer on a liquid surface we are in fact measuring the difference between the surface tension of a clean liquid surface and that of one covered by the monolayer, and referring to it as surface pressure ($\pi$) (equation I.1):

$$\pi = \gamma_0 - \gamma$$  \hspace{1em} (eq. I.1)

where $\gamma_0$ is the surface tension of the clean liquid and $\gamma$ is the surface tension of the film covered liquid surface.\textsuperscript{30} The surface tension of the film-covered liquid surface decreases as the molecules that compose the film become more ordered and tightly packed. Thus, an increase in surface pressure is actually a decrease in the surface tension of the film-covered water subphase.

Surface tension is also involved when choosing a solvent for spreading the material under study on the water surface. One of the requirements of the solvent is that it spreads on top of the subphase (light interference patterns are visible when this occurs). This information is provided by the "spreading coefficient", which is given by equation I.2:

$$S_{WA} = \gamma - \gamma_0 - \gamma_w$$  \hspace{1em} (eq. I.2)
where B is the solvent that is spreading over a subphase composed of A and $\gamma_{BA}$ is the surface tension at the interface between B and A. Spreading of the solvent will only occur for positive values of $S_{BA}$. It can be seen that for liquids with a high surface tension, such as water, the solvent is required to have a low surface tension for spreading to take place.

I.6. Hydrogen Bonding, the Hydrophobic Effect, and Hydrophobic Interactions

When a covalently bound hydrogen atom forms a bond to another atom, the second bond is referred to as a hydrogen bond. Hydrogen bonds can be either intramolecular or intermolecular. For intramolecular hydrogen bonding to occur A and B of A-H...B must be in a favorable spatial configuration. Hydrogen bonds play a particularly prominent role in water since each oxygen atom with its two hydrogens can participate in four such linkages with other water molecules: two involving its hydrogen atoms and two more with its unshared (lone-pair) electrons. The four hydrogen bonds around each water molecule form a nearly tetrahedral structure which extends into a three-dimensional network. This is not a static structure since the lifetime of each bond is estimated at $10^{-13}$s. The energy of the system is at its lowest when each water molecule forms the maximum number of bonds with its nearest neighbors.
The hydrophobic effect is the phenomenon observed when a nonpolar molecule or surface comes in contact with water molecules. The water must reorient in order to reduce its free energy. This disrupts the existing water structure, imposing a new, more ordered, structure on the surrounding water molecules; this is entropically unfavorable. The hydrophobic interaction arises from the hydrophobic effect and describes the unusually strong attraction between nonpolar molecules and surfaces in the presence of water. It is because of this that some materials form small "islands", in which the molecule’s hydrophobic chains are closely packed, even at surface areas where the films should be very expanded.

I.7. Film-Forming Materials

Most molecules carry no net charge, but many possess an electric dipole. The molecules that form monolayers at the air-water interface need to have a dipole. They must have a nonpolar part (usually a linear or branched hydrocarbon chain), and a polar (sometimes ionic) part. The strong interactions between the water molecules and the very weak interactions between the nonpolar group and water molecules tend to squeeze the nonpolar part out of the water, hence it is called hydrophobic. The polar part, on the other hand, interacts strongly with the water via dipole-dipole or
ion-dipole interactions and is solvated, hence it is called hydrophilic.\textsuperscript{23} The molecule as a whole is called an amphiphile.

I.8. Studies of Langmuir Monolayers

Approaches to the study of monolayers must be able to deal with the very small amount of material present. Even though the surface area of a Langmuir trough is substantial, the resulting film is only one molecule thick (a few nanometers) and typically consists of approx. 50 µg, or a few hundred nanomoles. When studying a monolayer film the probe of the characterization technique can be oriented perpendicular or parallel to the plane of the film.

I.8.a. Probing Perpendicular to the Film Plane

The extreme thinness of the monolayer makes it difficult to characterize it while it is at the gas-liquid interface. In this type of study, we are attempting to characterize a small portion of the film. Typically, the number of molecules sampled is insufficient to give a good signal to noise ratio. There have been a few instances where spectroscopic techniques were successfully used to monitor reactions involving monolayers at the gas-water interface. In one case a polymerization involved the disappearance of bonds that were easily observed in the UV/visible spectrum. A Langmuir trough was built into a UV-visible
spectrophotometer to enable direct observation of the polymerization of the monolayer. In a similar study, quartz optical fibers were used to guide the light from a spectrophotometer to the film under study and back to the detector. In another set of experiments the reflection of light from dye monolayers was measured, again using optical fibers. Only recently has FTIR been used effectively to study a film at the air-water interface, using reflection-absorption infrared spectroscopy (FTIR-RAS), where the water surface acts as the reflective element. However, highly modified Langmuir troughs were used and such studies are limited to films composed of molecules containing strongly absorbing chromophores.

One can bypass the problem of too little material by removing it from the interface and configuring it so that more of it will interact with the characterization technique. This re-structuring can be atactic, where the molecules lose the high degree of order present in the monolayer and attain a bulk-like disorder. Alternatively, the order present in monolayers can be preserved by forming multilayers, either via vertical dipping (Langmuir-Blodgett technique), or via horizontal lifting, or dipping. The most utilized spectroscopic characterization methods are FTIR and X-ray and electron diffraction. In the case of FTIR, Attenuated Total Reflectance (ATR) experiments provide a much better signal to noise ratio than regular transmission experiments. Even monolayer
coverage of the ATR prism can yield valuable information. When polarized radiation is used, the orientation of the molecules in the layers can also be determined."

Another technique that works well despite operating perpendicular to the monolayer plane is the surface potential measurement. In this approach the Volta potential between the liquid surface and a metal probe is monitored. The probe is coated with an α-emitter to ionize the air between it and the liquid. Extremely small variations in the surface potential can be detected by this method. The potential of the film-free surface is measured first and compared to that of the film-covered surface at various stages of compression." The great sensitivity of the technique allows it to be effective despite the very small number of molecules with which it interacts.

I.8.b. Probing in the Plane of the Film

A characterization technique that collects information in the plane of the monolayer has a much higher chance of success than one that works perpendicular to it, because it is interacting with many more molecules. The classical Langmuir film characterization techniques of pressure/area (π/A) isotherms (monitoring the changes in surface pressure as the molecular area changes while keeping the temperature constant), stress relaxation over time (keeping either the area or the surface pressure, as well as the temperature,
constant) and surface viscosity measurements fall into this category.

The $\pi/A$ isotherm (Figure I.8.1) is an XY plot which can provide a lot of information about the film. When the film is first spread on the subphase each molecule has a large amount of area available to it; it can attain its lowest energy conformation. There is very little surface pressure at this point (measurable only by extremely sensitive equipment) and the film is said to be in a gaseous state. During the measurement of an isotherm, as the
surface area of the trough is limited, the area available to each molecule is reduced. At some point neighboring molecules start getting pressed against each other, although they still have a broad range of conformations available to them. This leads to an increase in the surface pressure. The molecular area corresponding to this event is called the liftoff area; the film is now entering the liquid-expanded phase. The slope of the isotherm is small during this phase, i.e. large changes in molecular area produce small changes in the surface pressure. As compression continues, the film enters the liquid-compressed state. The change in surface pressure resulting from a change in the molecular area increases; the slope of the isotherm curve increases. Still, the molecules have a range of conformations available to them in this phase. Eventually the polar groups of the individual molecules are pressed up tightly against each other, with a very limited set of conformations available to the tails. This is referred to as the solid phase and a very small change in molecular area produces very large changes in the surface pressure. This is reflected by the very steep slope of the isotherm curve during the entire phase. The transition from liquid-compressed to solid phase is often very sharp, resulting in a prominent "kink" in the isotherm curve, which is termed the phase transition point. Phase transitions occurring at various points can also be observed as transition points, where there is a sudden change in the slope of the $\pi/A$ isotherm curve.
The molecular area when the individual molecules are packed as tightly as possible is termed the co-area and is derived by extrapolating the isotherm curve corresponding to the solid phase back to the X-axis. Eventually, as the molecular area is limited further, the pressure exerted by the closely packed molecules against each other overcomes the forces which keep them in a monolayer and the film collapses.

The stress relaxation experiment is performed by first compressing the film to a given surface pressure. At this point we can keep the pressure constant and monitor the rate of decrease of the molecular area. This is referred to as a creep test since the barrier "creeps" slowly to reduce the surface area and offset any decreases in pressure brought on by the slow collapse or restructuring of the monolayer. A film is said to be stable at a given pressure when it exhibits a slow rate of decrease of its molecular area with time. Alternatively, we can keep the area constant and monitor the rate of decrease of the surface pressure.

A viscosity measurement experiment attempts to determine the shear viscosity of a film (its resistance to flow). It can be done in two ways. One approach is to compress a film to a given surface pressure and then monitor the decrease in surface pressure as the film is allowed to flow through a long, narrow canal into a region of no surface pressure. A film that flows slowly through the canal, producing a slow rate of decrease of the surface pressure,
has a high surface viscosity. This type of measurement occurs over a pressure gradient and the shear rate of the film is not constant (it decreases with decreasing surface pressure). A second type of viscosity measurement, which does not have these limitations, consists of determining the damping of the oscillations of a torsion pendulum, disk, or ring, by the film.

I.9. Reactions in Organized Media

The chemical reactivity of a species present in a specific orientation and in a known and controlled microenvironment may be different from the reactivity of the same species present in the bulk phase. Previous studies in our research group and by others have indicated that such differences do in fact exist. As an introduction to our efforts to find such environment controlled effects in monolayers, a summary of some of the techniques used and results obtained in this area follows.

I.9.a. Reactions in Monolayers

A variety of reactions have been studied at the air/water interface. Among the first was the investigation of the alkaline hydrolysis of long chain esters. One report indicates that in an expanded film the rate of hydrolysis approximates that in the bulk solution, while in a compressed film it is slowed down, presumably due to changes in the molecular orientation. Another report
Figure I.9.1. Tripalmitin hydrolysis, from reference 39.

studied tripalmitin hydrolysis (Figure I.9.1) and found that the hydrolysis of dipalmitin, in the monolayer environment, is slower than that of monopalmitin and tripalmitin, resulting in a
dipalmitin-rich monolayer." A third report, studied the hydrolysis of tris(2,2'-bipyridine)ruthenium (II)\(^3\). Here again, the concentration of the partially hydrolyzed product was found to initially increase (it comprises 75% of the hydrolyzed product after the first 20 min. of reaction) and subsequently decreases with time. In this report the rate of hydrolysis was found to be faster than that observed in the bulk reaction.\(^4\)

In a study of the enzymic hydrolysis of lecithin monolayers by snake venom, the rate determining factor was found to be the degree of unsaturation of the lecithin's fatty acyl chains. Higher degrees of unsaturation do not allow efficient packing of the hydrophobic chains in the monolayer, thus increasing intermolecular spacing, which in turn increases the rate of hydrolysis.\(^5\)

The esterification of a polymerized acid monolayer with an alcohol that is dissolved in the subphase was shown to proceed nearly to completion. This occurred despite the fact that the water in the subphase should re-hydrolyze the ester formed, under the acidic conditions employed in this reaction.\(^6\) The alcohol used in this reaction (benzyl alcohol) is slightly water soluble and thus is concentrated at the interface. The reaction is thought to proceed due to the ordering of the polymerized acid monolayer and the concentration of the slightly soluble alcohol at the interface.

The cyclization of nerol is promoted by an acidic subphase and occurs only for expanded films where the molecule can attain the
conformation necessary for the reaction to proceed. Similarly, the acid catalyzed dehydration of 1,1-diphenyl-1-octadecanol occurs 20 times faster in very expanded monolayer films than it does in compressed films.

The polymerization of oriented monolayers has been studied in an attempt to achieve the highest degree of ordering of the resulting polymer. It was found that the UV-initiated polymerization of octadecyl methacrylate in a condensed film was faster than that in an expanded film.


The problem of determining what is actually occurring during a reaction in a Langmuir film is not an easy one to solve. The major difficulty arises from the very small amount of material present. Ideally, we would like to study the transformations that the surfactant molecules are undergoing without perturbing the film (while it is still at the air-water interface). Changes in film behavior could be used to attempt an explanation of the changes occurring at the molecular level. As long as a standard Langmuir trough is utilized however, the information that can be obtained while the monolayer is at the air-water interface is limited to \( n/A \) isotherms, viscosity and surface potential measurements, and stress relaxation experiments. Information obtained in this manner can give us the area per molecule, the film's resistance to flow, its
cohesiveness, and a measure of its rigidity, but it cannot identify the actual chemical composition of the molecules which make up the film.

In our work, we supplement the in-situ film characterization by recovering the film-forming material from the air-water interface and attempting to analyze it. The problems are the small amount of material and the difficulties of efficient material recovery. Over the years, a number of solutions have been proposed.

One solution is to combine the products from a number of experiments to yield enough material so that conventional analytical techniques can be utilized. The combined products are then analyzed. This technique combines the material produced by a number of reactions. This can lead to indeterminate errors, if variations exist from one reaction to the next.

Another approach utilizes radioactive labelling of the starting material. Even when the amount of recovered material is small, the high sensitivity of a radioactivity detector makes it unnecessary to repeat the experiment and combine the recovered material. This technique presents several drawbacks as well, not the least of which are the precautions necessary due to the high radioactivity content that is required in the starting material. Others include the fact that only labelled products will be
detected and the extent of label incorporation must be unambiguously known for quantitation to be possible.

We have been referring to "removal" of the monolayer material from the interface, without discussing the details. One of the first methods used was to collapse the film to the smallest possible area and then "scoop" or "scrape" it off the water surface." This method however does not work well with non-rigid films and there is poor recovery of the monolayer material. Another method consists of aspirating the film off the interface and recovering it from the aspirator trap." The film quality does not affect this technique, but the extent of material recovery cannot be precisely anticipated.

A third method is to remove a small sample of the film without disturbing the rest of the monolayer." A sufficiently sensitive detector is required for this to be effective. This technique has been used in conjunction with a highly radioactive film.

A recovery technique that is more efficient than all of the above is that which utilizes the multicompartemntal Langmuir trough." In such a trough the film can be transported over the water subphase, onto a compartment filled with an organic solvent, such as hexane. The film is then dissolved in the solvent and near-quantitative recovery is possible.

After the film is recovered, spectroscopic and chromatographic techniques can be utilized for the analysis. Spectroscopic
techniques can be very sensitive, but may not differentiate among various products that may be present. Chromatographic techniques, on the other hand, can separate the various products present in the recovered material, but may not be as sensitive, depending on the material being analyzed and the detector used. If any unexpected products are formed, they might not be observed, depending on the conditions and the type of chromatography utilized.
Chapter II. Structure and Reactions in 1-Diazo-2-oxoalkane

Monolayers

II.1. Introduction

II.1.1. Chemistry of Diazo Compounds

Reactions involving diazo compounds can proceed thermally or photochemically. There are three pathways that the thermal decomposition of diazo compounds can follow. The first is a

\[
\begin{align*}
R' & \quad - \quad - \quad + \quad C^\bullet \quad N=\quad N \\
R^* & \quad \triangle \quad \rightarrow \quad R' \quad - \quad C^\bullet \quad + \quad N=\quad N \\
& \quad R^*
\end{align*}
\]

Figure II.1.1. Thermal carbene formation.

\[
\begin{align*}
R' & \quad - \quad - \quad + \quad C^\bullet \quad N=\quad N \\
R^* & \quad \triangle \quad \rightarrow \quad R' \quad - \quad C^\bullet \quad + \quad N=\quad N \\
& \quad R^*
\end{align*}
\]

Figure II.1.2. Azine formation.

24
unimolecular reaction leading to nitrogen and a carbene (Figure II.1.1). The second is a bimolecular decomposition leading to azines (Figure II.1.2). Finally, there is a third possibility in which acids can react with the diazo compound before loss of nitrogen" (Figure II.1.3).

\[
\begin{array}{c}
\text{X} - \text{H} \quad \overset{\text{R}^*}{\text{C}} \quad \overset{\text{N}}{\text{N}} \\ \\
\rightarrow \quad \text{X} \quad \overset{\text{R}^*}{\text{H}} \quad \overset{\text{C}}{\text{N}} \quad \overset{\text{N}}{\text{N}} \\
\end{array}
\]

\[
\begin{array}{c}
\text{X} \\
\overset{\text{H}}{\text{C}} \quad \overset{\text{R}^*}{\text{N}} \quad \overset{\text{N}}{2} \\
\end{array}
\]

**Figure II.1.3.** Acid-catalyzed decomposition.

\[
\begin{array}{c}
\text{R}^* \quad \overset{\text{C}}{\text{N}} \quad \overset{\text{N}}{\text{N}} \\
\overset{\text{R}^*}{\text{C}} \quad \overset{\text{A}}{\text{N}} \quad \overset{\text{hv}}{\text{hv}} \quad \overset{\text{R}^*}{\text{C}} \quad \overset{\text{N}}{\text{N}} \\
\end{array}
\]

**Figure II.1.4.** Diazirine formation.

The photochemical reaction of diazo molecules can follow two pathways. The first is nitrogen elimination, leading to a carbene (analogous to the thermal carbene formation). The second is a reversible rearrangement to the diazirine (Figure II.1.4). In
general, the longest possible wavelength is used for diazirine formation, with shorter wavelengths leading to carbene. Either the diazo or diazirine compound can be a carbene precursor.

![Figure II.1.5. Carbene reactions.]

Once a carbene is formed, a variety of further reactions are possible. It can insert into C-H and O-H bonds, as well as adding to olefins (Figure II.1.5).

II.1.2. Chemistry of Diazoketones

Apart from the general diazo compound reactions described above, diazoketones can undergo a unique reaction. It involves rearrangement of the diazoketone with loss of nitrogen, leading to a ketene (Figure II.1.6). This is known as the Wolff rearrangement and has two important applications: the homologation of carboxylic acids (Arndt-Eistert reaction), and the ring contraction of cyclic 1-diazo-2-oxo compounds. This second
Figure II.1.6. Ketene formation and applications of the Wolff rearrangement.

Figure II.1.7. Ketene reactions.
application can give rise to unusual strained ring systems\textsuperscript{2} (Figure II.1.6).

When a carbene is formed from a diazomethyl ketone molecule, it can undergo a carbene reaction or it can rearrange into a ketene. A ketene is also a very reactive species. It can dimerize or undergo reaction with nucleophiles that may be present (Figure II.1.7).

II.1.3. Background on Carboxylic Acid Monolayers

Langmuir films of long chain fatty acids were among the first studied. The only requirement for film formation is that the acid possess a suitably long hydrocarbon tail. The fatty acid with the shortest tail that forms solid monolayers is hexadecanoic (palmitic) acid. Pentadecanoic acid forms films which never actually attain a solid phase at room temperature.\textsuperscript{3} Palmitic and all higher homologous fatty acids form stable, high quality, Langmuir films, with tight packing of the individual molecules.

All fatty acid isotherms have a few common, distinctive, characteristics. The liftoff area is larger than expected for molecules containing only one saturated hydrocarbon tail and the liquid phase of the isotherm also lasts longer than expected. Both these observations indicate that there are interactions present even when the molecules have significantly more space than the co-area available to them. There is also a sharp transition point
between the liquid and solid phases at the fairly high surface pressure of approximately 25 dynes/cm.

The fatty acid film creep test stability is not consistent with the high degree of order suggested by their isotherms. Although the films display some resistance to collapse, it is evident that they are only moderately stable. The fatty acid film is in the liquid state under usual creep test surface pressures. This allows its constituent molecules a range of motions. Because of this, it can be presumed that extensive reorganization of the molecules is easily achieved in the fatty acid film, whereas this would not be so facile for molecules constrained in a solid-like film.

II.1.4. Films of 1-Diazo-2-oxoalkanes

Long-chained 1-diazo-2-oxoalkanes (DOA) resemble carboxylic acids with an equally long alkyl chain, in which the hydroxyl group has been exchanged with a diazomethyl group (-CHN$_2$). Extrapolating the behavior of carboxylic acids to DOA molecules, one would expect those that contain 15 and 17 carbons in their hydrocarbon tails, 1-diazo-2-oxoheptadecane (DOH) and 1-diazo-2-oxononadecane (DON), to behave similarly to hexadecanoic (palmitic) and octadecanoic (stearic) acid, respectively.
II.1.5. Photolysis of 1-Diazo-2-oxoalkane Films

Surfactants containing the 1-diazo-2-oxo functionality have previously been synthesized and some aspects of the photolysis of their films have been studied by Ringsdorf,\textsuperscript{a} Holden\textsuperscript{b} and coworkers. 1-diazo-2-oxopentadecane, 1-diazo-2-oxononadecane, 1-diazo-2-oxoheneicosane and 1-diazo-2-oxononacosane were photolyzed at a fixed molecular area (close to, but less than, the liftoff area). The films resulting from multiple experiments with the same compound were recovered and combined. This combined product was analyzed by IR and mass spectrometry. The analysis indicated the presence of carboxylic acid, formed from the addition of water to the ketene, and \(\beta\)-lactone, formed from dimerization of the ketene (Figure II.1.8). No evidence was found for the presence of the \(\alpha\)-
hydroxy ketone which would be formed from insertion of the
unrearranged carbene into water. On irradiation, the collapse
pressure of the film increased and its surface area became smaller.

Our work on the photolyses of DOA's focussed on two issues.
Firstly, could a more careful analysis of the photolyzate give
evidence for products other than carboxylic acid and ketene dimer?
Secondly, what is the dependence of the photolysis (if any) on
variations in surface pressure?

II.2. Experimental

II.2.1. General

NMR spectra are reported in units n, were recorded on a Varian
XL-200 spectrometer in CDCl₃, solvent and are referenced to CHCl₃ at
7.24 ppm. Infrared spectra were recorded on a Perkin-Elmer 1600,
or a Mattson Cygnus 25 FTIR operating at a resolution of 4 cm⁻¹. A
60 µL liquid cell (NaCl) was utilized and the material was
dissolved in CCl₃. GC-IR spectra were recorded on a Mattson
Sirius 100 infrared spectrometer operating at 4 cm⁻¹ and equipped
with a Cryolect matrix isolation sample collection facility
operating at 8 K. The outlet of a Kratos GC utilizing a DB5 column
was connected to the Cryolect. HPLC used a Waters 590 pump
equipped with a Rheodyne 7125 injector and a Waters 401
Differential Refractometer. Rainin Dynamax HPLC columns (Rainin
Instrument Co., Inc., Woburn, MA) were used in all separations.
Analytical columns had a 4.6 mm ID, while preparative columns had a 21.4 mm ID and all were 25 cm long. Regular phase (Si) columns were packed with 8 μm irregular silica (60 A pore size) and reverse phase (C<sub>18</sub>) columns contained the same type of silica coated with C<sub>18</sub> material. TLC was performed on aluminum-backed 0.2 mm 60F254 plates from EM Science utilizing phosphomolybdic acid as a visualization agent. Dry THF was distilled from Na metal. Ether was distilled before use. HPLC grade CH<sub>2</sub>Cl<sub>2</sub> (Fisher) was used as received. HPLC grade hexane, ethyl acetate (EtOAc), 2-propanol (IPr) and methanol (Fisher) were used as received for preparative and analytical HPLC. Water was doubly distilled. Thionyl chloride (Aldrich) was distilled under N<sub>2</sub> and stored tightly capped until needed. Benzene (Fisher, certified) was distilled and stored under N<sub>2</sub>. Diazald (N-methyl-N-nitroso-p-toluenesulfonamide; Aldrich) and KOH pellets were used as received. H<sub>2</sub>SO<sub>4</sub> and glacial acetic acid (Fisher) were used as received. Hexadecanoic, heptadecanoic and nonadecanoic acids (Aldrich, 99% purity) were recrystallized twice from diethyl ether before use. Octadecanoic acid (Fluka, 99+% purity) was analyzed, found to be free of contaminants, and was used without further purification.

Tetraethylammonium perchlorate (TEAP) (GFS chemicals, Columbus, OH) which was used as the electrolyte when performing Liquid Chromatography with an Electrochemical Detector (LC/EC) was purified as follows. The material was recrystallized from 50%
ethanol:water, followed by filtration and air-drying in a nalgene funnel (glass funnels are to be avoided, as the grinding of TEAP crystals against them during the air-drying process can lead to an explosion). The air-dried material was further dried under vacuum in a drying pistle, which was bathed in refluxing 95% ethanol : water. Finally, the dried material was stored in a desiccator until it was needed.

II.2.2. Surfactant Synthesis

II.2.2.1. Octadecanoyl Chloride

The procedure of Hixson and Hixson

for the preparation of acid chlorides from p-azidobenzoic acids was used without modification. Octadecanoic acid (1 g, 3.52 mmol) was added to freshly distilled SOCl₂ (13 mL, 21.2 g, 178.2 mmol) in an oven-dried 50 mL round bottom flask equipped with a magnetic stirring bar and a reflux condenser and allowed to reflux under nitrogen for 1/2 h. The excess thionyl chloride was distilled from the solution. When most of the excess SOCl₂ solution had been removed, freshly distilled benzene (10mL) was added and then removed by distillation. This process was repeated one more time to ensure that most of the thionyl chloride had been removed. (If this distillation is carried-on too far the liquefied product is transformed into a black tar.) The acid chloride was then fractionally distilled under vacuum (0.02 mm Hg, Kugelrohr
apparatus) and obtained as a viscous colorless liquid; yield 0.94 g (88%); \( ^1H \text{ NMR} 0.88 \, (t, \, 3H), 1.26 \, (m, \, 28H), 1.63 \, (m, \, 2H), 2.76 \, (t, \, 2H); \text{IR} \, 2927, \, 2855, \, 1711, \, 1552, \, 1253 \, \text{cm}^{-1}. \) Literature \(^7 \) \( ^1H \text{ NMR} \) values 0.87 \( (t) \), 1.23 \( (m) \), 1.74 \( (m) \), 2.8 \( (t) \).

Hexadecanoyl chloride was prepared in a similar manner from hexadecanoic acid; yield 86%; \( ^1H \text{ NMR} 0.85 \, (t, \, 3H), 1.23 \, (m, \, 24H), 1.70 \, (m, \, 2H), 2.88 \, (t, \, 2H); \text{IR} \, 2925, \, 2856, \, 1801, \, 1466, \, 1406 \, \text{cm}^{-1}. \) Literature \(^7 \) \( ^1H \text{ NMR} \) values 0.87 \( (t) \), 1.27 \( (m) \), 1.8 \( (m) \), 2.9 \( (t) \).

II.2.2.2. 1-Diazo-2-oxononadecane

A solution of Diazald (5.5 g in 50 mL of distilled ether) was added dropwise to a mixture of aqueous base (2.5 g KOH in 4 mL H\(_2\)O), distilled ether (8 mL) and 2(2-ethoxyethoxy)ethanol (14 mL) at 64 \( ^\circ \text{C} \) in a mini-diazald kit (Aldrich Chemical Co.). A dilute solution of diazomethane (18.1 mmol) in diethyl ether was prepared in this manner and was kept at 0\( ^\circ \text{C} \). A magnetic stirring bar was added to the flask and a solution of octadecanoyl chloride (1.83 g, 6.03 mmol in 10 mL distilled ether) was added dropwise, with stirring, to the approximately three-fold molar excess of the chilled diazomethane solution. The mixture was allowed to stir at 0\( ^\circ \text{C} \) for 1/2 h in subdued light, before being warmed to room temperature. The excess diazomethane was quenched with dropwise addition of glacial acetic acid and the volatile components were evaporated under reduced pressure. Warm diethyl ether was used to
recrystallize the pale yellow needle clusters two times; mp 53.9-54.7 °C; yield 1.65 g (90%); $^1$H NMR 0.85 (t, 3H), 1.23 (m, 28H), 1.62 (m, 2H), 2.30 (t, 2H), 5.20 (s, 1H); IR 2927, 2855, 2106, 1655, 1362 cm$^{-1}$. Literature $^a$ $^1$H NMR values 0.90 (t, 3H), 1.27 (m, 30H), 2.30 (t, 2H), 5.23 (s, 1H).

1-Diazo-2-oxoheptadecane was prepared from addition of hexadecanoyl chloride to a dilute CH$_2$N$_2$ diethyl ether solution in a similar manner to yield pale yellow platelets; mp 59.8-61.0°C; yield 91%; $^1$H NMR 0.90 (t, 3H), 1.29 (m, 24H), 1.60 (m, 2H), 2.31 (t, 2H), 5.21 (s, 1H); IR 2927, 2855, 2106, 1654, 1358 cm$^{-1}$. Both of these materials were stored in foil-covered vials at -5°C.

II.2.2.3. 2-Oxo-nonadecanol

A solution of 1-diazo-2-oxononadecane (70 mg; 0.23 mmol) and concentrated H$_2$SO$_4$ (50 µL) in 55 mL of 25% water in 1,4-dioxane were heated to reflux in a 100 mL flask equipped with a stirring bar and a reflux condenser for 4 h. The dioxane was evaporated under reduced pressure and the mostly aqueous solution was extracted with diethyl ether. The combined ether extracts were dried over Na$_2$SO$_4$, and evaporated under reduced pressure. The white powder obtained was recrystallized from hexane; mp 66.2-67.0 °C; yield 55 mg (80%); $^1$H NMR 0.85 (t, 3H), 1.23 (m, 28H), 1.56 (m, 2H), 2.38 (t, 2H), 3.08 (t, 1H), 4.22 (d, 2H); IR 3500, 2927, 2855, 1721, 1466, 1276, 1063 cm$^{-1}$.
2-oxo-heptadecanol was prepared from 1-diazo-2-oxo-heptadecane in a similar manner. White powder; mp 70.8-71.3°C; yield 84%; 1H NMR 0.85 (t, 3H), 1.23 (m, 24H), 1.61 (m, 2H), 2.36 (t, 2H), 3.08 (t, 1H), 4.22 (d, 2H); IR 3498, 2928, 2855, 1722, 1466, 1058 cm⁻¹.

II.2.2.4. Purity of Compounds used for Film Formation

Even after a few recrystallizations, analytical HPLC detected contaminants in most of the materials that were to be used for film formation. Final purification of these compounds was by preparative HPLC, first by reverse-phase (C₈) and then normal-phase (Si) chromatography. Retention times using the preparative C₈ column with 2% H₂O/methanol @ 15 mL/min: OHD 9.4 min., DOH 11 min., C₇ acid 12.3 min., OND 12.8 min., DON 14.8 min., C₉ acid 18.5 min. Retention times using the preparative Si column with 20% EtOAc/hexane @ 15 mL/min: C₇ acid 7.5 min., C₉ acid 8 min., DON 9.4 min., DOH 10 min., OHD 14.6 min., OND 15 min. Reinjection of these materials into the HPLC showed them to be free of contaminants. Retention times using the analytical C₈ column with 2% H₂O/methanol @ 1 mL/min: OHD 6.8 min., DOH 7.6 min., C₇ acid 9.2 min., OND 9.5 min., DON 10.6 min., C₉ acid 12.5 min. Retention times using the analytical Si column with 20% EtOAc/hexane @ 1 mL/min: C₇ acid 5.2 min., C₉ acid 5.5 min., DON 6.3 min., DOH 6.7 min., OND 9.8 min., OHD 10.2 min.
II.2.3. Monolayer Formation and Characterization

The single largest concern when working with monolayers at the air-water interface is to ensure that no surface-active contaminants are present. This includes not only the state of the actual compounds that will be studied, but also all glassware and other equipment that will be used in the experiments.

II.2.3.1. Clean Room

The facility where all the monolayer work was performed is the Polymer Microdevice Laboratory (PML). This is a Class-100 laboratory which is equipped with Class-10 laminar flow hoods (designed by Environmental Air Control, Inc., Hagerstown, MD). The Langmuir troughs are located inside the laminar flow hoods. The Class-# rating is an indication of the number of particles per square foot in a given area. To maintain the high degree of cleanliness reflected by these ratings, the entire laboratory is under a positive air pressure and all air is recirculated, after it is passed through appropriate filters.

Any personnel wishing to use the facility must first don clean-room hoods, coveralls and boots (approved for Class-100 environments) in the semi-clean changing room. Sticky mats inside and outside the entrance ensure that no dirt is tracked into the main laboratory. In addition, clean-room gloves and masks (approved for Class-10 environments) are used when working over or
near the troughs. All light in the PML is ultraviolet-filtered, to avoid decomposing ultraviolet-sensitive materials.

II.2.3.1.a. Film Balance and Accessories

The Langmuir troughs used are Lauda M.G.W. Model P (manufactured in W. Germany). They are channelled on their underside, to allow thermostated water to be recirculated through them (Fisher Scientific; Model 90 recirculator bath) and maintain a fixed temperature. Their dimensions are 70 x 15 x 0.6 cm and they are equipped with a 3 x 8 cm dipping well, which extends 6 cm below the trough surface. A computer-controlled mechanical dipper can be programmed to allow transfer of monolayers to a solid support. A movable barrier is provided for monolayer manipulations and a fixed float is attached through a Linearly Variable Differential Transformer (LVDT) to an IBM-XT personal computer (PC). This allows continuous monitoring of the surface pressure exerted by the monolayer (Figure II.2.1). The PC also monitors the location of the movable barrier and stores data during an experiment. Details of the interface and software used for the interaction of the PC with the Lauda balance are provided elsewhere. The balances are also equipped with a temperature sensor, which constantly monitors the temperature of the subphase. It is located behind the pressure transducer in an area of the trough where it does not interfere with the film. All components that come in contact with the
Figure II.2.1. Lauda film balance.

aqueous subphase or the monolayer are solid teflon or fluoropolymer-coated, to ensure their hydrophobicity and oleophobicity.
Cleanliness of the trough was ensured by wiping everything that came in contact with the monolayers or with the aqueous subphase with chloroform-soaked Class-100 wipers (Berkshire Corp., Great Barrington, MA), followed by rinsing with copious amounts of purified water (see below). The troughs are encased in a container equipped with a hinged lid to provide additional security from airborne contaminants and allow for easier temperature equilibration. The film balances are placed on vibration-isolation setups to dampen environmental vibrations which can perturb the Langmuir films.

In order to do the surface viscosity measurement experiments, three canal viscosimeters had to be fabricated. A block of virgin teflon was purchased (Aetna Plastics, E. 11 & St. Clair, Cleveland) and two rectangular pieces measuring 8 x 1/2 x 1/2 in. and a third measuring 8 x 1/2 x 3/4 in. were machined from it (C.W.R.U. machine shop). A canal measuring 1/2 x 1/4 in. was cut in the middle of each viscosimeter. The canal width was 1/8 in. in the first, 1/16 in. in the second and 1/32 in. in the third viscosimeter (Figure II.2.2). The viscosimeter with the 1/32 in. canal width is wider than the other two, which means that its canal is longer.

II.2.3.1.b. Water Purification System

Langmuir films are formed at the air-water interface and therefore the purity and cleanliness of the water used is critical
Figure II.2.2. Viscosimeter dimensions.

to the quality of the films that are obtained. A commercial water purification system could have been used to remove particulate matter and ionic contaminants from the water. However, a home-built system was assembled instead, in order to avoid the release of surface-active organic compounds that is observed from the ion-exchange resins employed in many commercial systems. It utilizes the following in series: 1) a pair of water softeners which alternately work or regenerate every 12 hours, 2) a series of
filters (to remove particulate matter), activated carbon cartridges (to remove organic compounds) and more filters (to remove carbon fines downstream from the carbon cartridges) and 3) a reverse osmosis setup. At this point the treated water enters a quartz distillation setup, while it is bubbled with nitrogen. The condensed water is carried through all-teflon tubing to a teflon solenoid valve. If the resistivity of the water is above a given value, the solenoid valve closes and the water is collected in an all-teflon holding tank, if not, the valve opens and the water is diverted to a rinse tank. The holding tank is operated under continuous overflow conditions to ensure that no surface active material, which may have been leached from the tank, or the tubing, remains in it. Finally an ultraviolet lamp is built into the spigot, to ensure that no bacteria can migrate through it, to the holding tank. Water with a minimum resistivity of 17.5 megohms/cm is obtained in this manner." 

II.2.3.1.c. The Subphase

The aqueous subphase used in most experiments consisted of PML-purified water, obtained as described above. Its pH was in the range of 5.5-6.0, due to absorption of CO₂ from the air. When filling the balance with water, a positive meniscus is formed with the subphase level located 1-2 mm above the lip of the trough.
II.2.3.1.d. Glassware Cleanliness

All glassware used in the PML was thoroughly cleaned following
the "standard degrease" procedure outlined below. They were
subjected to ultrasonication for 5 minutes in each of the following
series of "electronic grade" solvents, in order: trichloroethylene,
acetone, methanol. Following this, they were oven-dried inside the
PML, at 60°C, for approx. 12 hours. After this, they were placed
in Class-100 bags until needed. The glassware and teflon tubing
used for the recovery of the films prior to GC analysis had to be
"acid-washed" to ensure that no fatty acid product was lost due to
interactions with basic sites in them. An "acid-wash" consists of
attaching the apparatus to a vacuum source and aspirating/washing
with the following in the sequence given: acetone, 0.025 M HCl,
doubly distilled water, acetone and finally hexane.

II.2.3.1.e. Spreading Solutions

The method by which the monolayers of the various compounds
are prepared, is by dissolving the material in a suitable solvent
and spreading some of this solution on the water surface. The
solvent chosen for this study was HPLC-grade chloroform (Fisher
Scientific, containing 1.2% EtOH), for the reasons listed below: 1)
It is free of surface-active impurities; i.e. spreading only
chloroform on the subphase and compressing fully, produced no
detectable pressure rise. 2) It spreads completely on the water
surface. 3) It readily dissolves all the compounds used in the study. 4) It does not evaporate so quickly that the concentration of the solutions changes during solution transfers.

The solutions were prepared in Class A Pyrex 25-mL volumetric flasks, capped with ground glass stoppers which were "standard degreased" as described above. This volume was chosen so that the solution would be dilute enough (approx. 0.5 mg/ml) to allow for proper spreading of the monolayer material, while still maintaining acceptable precision when weighing-out the material. The surfactants (10-15 mg) were weighed (Mettler Model AE 163 balance, accuracy +0.1 mg) into the tared volumetric flask. Static electrical charges can make this operation very difficult and every attempt was made to eliminate them. These charges arise from rubbing between the plastic clean-room coveralls and the plastic chairs and are aided by the low relative humidity (35-40%) in the PML. Grounding of the operator with a conductive wrist-strap and wrapping the sample vial and the volumetric flask with aluminum foil eliminated the static charges outside the balance chamber. 44 A StaticMaster brush (contains a small amount of Polonium of low radioactivity; an α-particle emitter) was kept inside the balance chamber at all times and aided in dissipating any charges in it.45,46 After the desired amount of material was added, the flask was filled with chloroform and the weight of the solvent was determined. (This was found necessary as the accuracy of the
volumetric flasks was compromised due to the expansion/contraction cycles they were subjected to during the standard degrease procedure). From the weight of the solvent and the density at room temperature (1.472 g/mL), the volume of chloroform in the volumetric flask was determined, which gave an accurate value for the concentration of the material in the solution. Volumetric flasks containing HDMK solutions were wrapped in aluminum foil to prevent accidental photolysis during experiments involving ultraviolet irradiation of the monolayers. All solutions were stored at 5 °C when not in use and were allowed to equilibrate to room temperature before spreading.

II.2.3.2. Procedures for Film Formation

Before the films were formed, the subphase temperature was allowed to equilibrate with the recirculating bath. In the experiments described here the temperature was kept at 19.0±0.1 °C (unless otherwise noted). The pressure transducer was then calibrated, using a single weight and five points on the calibration curve.

The barrier location formula that is used by the PC to determine the barrier position was periodically updated by performing a position calibration. To do this, the barrier is moved to any location on the trough and the PC prompts the operator for the barrier position. This is read off a scale which is
permanently fixed next to the trough, entered, and the barrier moved to a new location, where the same operation is repeated. After several barrier locations are thus entered, the PC constructs the best fit between the barrier position data points and the voltages that correspond to each position. (The voltages are obtained from a rheostat that is a part of the movable barrier assembly.) It can then pinpoint the barrier position based on the voltage it is reading at any given location.

To form a Langmuir film, the surfactant solution (10-90 µL) was spread on the subphase using a Hamilton Gastight volumetric syringe (Hamilton Co., Reno, NV) of either 100 µL or 50 µL capacity. The area allotted for the expanded monolayer material was 3-4 times the area at which a surface pressure is first detected (the point at which the π/A curve starts to rise from the baseline during an isotherm). The solvent was then allowed to evaporate for 4-6 min. Monolayer compressions were performed by moving the barrier at a fixed velocity of 1.2 cm/min. This corresponds to a change of approximately 2 Å²/molecule/min.

II.2.3.3. Procedure for π/A Isotherms

To determine a pressure/Area (π/A) isotherm, the film is compressed at the steady rate mentioned above until the collapse of the monolayer is detected. When working with a film which is not expanded (i.e. a film which was photolyzed compressed), the area
available to the film is first expanded to 2-3 times the co-area. This serves to allow the molecules enough space to obtain their lowest energy conformation. The steady compression mentioned above follows this action. The PC collects data points for elapsed time, barrier location and surface pressure during the steady compression of the film. The operator enters the values for the molecular weight, the solution concentration and the amount of solution that was spread. The PC then calculates the molecular area at a given point by using the barrier position corresponding to that point, in conjunction with the quantities supplied by the operator.

II.2.3.4. Procedure for Creep Tests

For creep tests (study of the variation in molecular area over time, at constant surface pressure), the steady compression mentioned above was also used. The automatic surface pressure controller was engaged after the surface pressure rose above zero. This maintained the surface pressure at the preset value by varying the area available to the film to compensate for events which caused changes in the surface pressure. The pressure for all the creep tests reported is 2 dynes/cm, unless otherwise noted. During a creep test, the PC collected the same data points that were described above after the automatic pressure controller was engaged.
II.2.3.5. Procedure for Viscosity Measurements

The canal viscosimeter method has previously been utilized to measure the surface shear viscosity of films.\textsuperscript{m,22} In those instances however, the pressure differential at the ends of the canal was maintained constant. The film viscosity at a single surface pressure differential was measured in this way. Finding the maximum shear viscosity of a film was then reduced to attempting the measurement over a wide range of surface pressure differentials. In the modification of the method that we have used, the surface shear viscosity corresponding to an entire range of surface pressure differentials can be obtained in a single experiment. More importantly, there is a continuous measurement of the viscosity, ensuring that the maximum is not accidentally overlooked. Films of varying viscosity and specific surface pressure ranges can be studied by choosing the appropriate canal width.

For viscosity measurements, the canal viscosimeter with the appropriate canal width was placed in front of the movable barrier (with the canal edges in contact with the subphase) before the solution was spread onto the surface. Then, during monolayer compression, it was pushed in front of the movable barrier. When the surface pressure reading reached the target value (30 dyn/cm), the movable barrier was stopped. As quickly as possible, the movable barrier expansion velocity was set to its maximum value.
Figure II.2.3. Viscosimeter positioning on the trough.

(7.2 cm/min), barrier expansion was started (leaving the viscosimeter in place), and data collection with the PC was also started. After the movable barrier was sufficiently far from the viscosimeter (when the area between viscosimeter and movable barrier was approx. two times the area between viscosimeter and pressure transducer), the expansion of the movable barrier was stopped (Figure II.2.3). Data collection with the PC was continued until the surface pressure reached zero, or the slope of the surface pressure vs time curve showed too small a rate of decrease to conveniently monitor it further.

A semi quantitative understanding of the surface viscosimetry data was achieved with a computer program written by Prof. J. A.
Mann (Chemical Engineering, C.W.R.U.). He constructed a working formula for determining the surface shear viscosity. This program, written in APL (A Programming Language), combines the data from a \( \pi/A \) isotherm and a surface viscosity measurement for a given film. It was run on an EPS Technologies computer equipped with an 80386 microprocessor operating at 20 MHz.

The first step is to take the derivative of the pressure over the area from the \( \pi/A \) isotherm data from which \( k_e \) (the film's elastic modulus) can be calculated (eq. II.1).

\[
k_e = -A \left( \frac{d\pi}{dA} \right) \quad \text{(eq. II.1)}
\]

The \( k_e \) vs \( \pi \) plot is constructed after performing a polynomial fit to "smooth" the data. The steepness of the \( \pi/A \) isotherm curve is an indication of how compressible the film is; a steeper slope indicating a less compressible film. One can use \( k_e \) to quantitate the film compressibility \( (c_t) \) (equation II.2).

\[
c_t = 1/k_e \quad \text{(eq. II.2)}
\]

Following this, the viscosimetry data (\( \pi \) vs \( t \) for a given slit geometry) are used to calculate the derivative of the pressure over time (\( d\pi/dt \)) and construct the \( \pi \) vs \( d\pi/dt \) plot. The values for the area of the film \( (A) \), the canal length \( (l) \), and canal width \( (a) \) are then supplied and the program calculates the surface shear viscosity \( (\eta) \) (equation II.3). In this equation, \( \pi(0,t) \) is the spreading pressure of the film at the inlet of the canal \( (l = 0) \); it is assumed that the spreading pressure beyond the canal is
essentially zero, \( \tau(1,t) = 0 \). The plot of shear viscosity vs \( \tau \) is then generated.

\[
\eta = -\frac{2}{3}(a^2/1) \tau(0,t) \left( 1/((A/k_c)(d\tau/dt)) \right) \quad \text{(eq. II.3)}
\]

II.2.4. Monolayer Reactions and their Analysis

II.2.4.1. Photolysis of Langmuir Films

UV-sensitive films were photolyzed with varying amounts of area available to each molecule. There are two general categories that describe the state of the film during the photolysis, expanded and compressed.

In expanded film photolyses the film displays no surface pressure; the molecules have more space than the co-area available to them and exert no measurable pressure on their neighbors. The relative area available to each molecule is described in terms of a multiple of the co-area. Expanded photolyses were performed at 4x, 30x and 100x the co-area. Since the co-area is approximately 20 A^2/molecule, the molecules had approximately 80, 600 and 2000 A^2/molecule available to them at the above conditions.

In compressed film photolyses the molecular area is fairly constant and close to the co-area; the surface pressure in the film varies however. Compressed photolyses were performed at 2 (liquid state) and 30 (solid state) dynes/cm.

For 30x and 4x co-area expanded films, the appropriate amount of solution was spread over the maximum available area on the
trough. For compressed films at 2 and 30 dyn/cm the film was
compressed after the solution was spread and the automatic pressure
control was engaged, keeping the pressure constant throughout the
photolysis. The balance lid was opened before starting the
photolysis. A hand-held 0.16 Amp., 254 nm, UV lamp (Ultra-Violet
Prod. Inc., San Gabriel, CA; Model UVG-54) was used for all
photolyses. The lamp was held at a distance of approximately 6 in.
above the film and was slowly moved over the entire area occupied
by the film. The photolysis of the films is accompanied by changes
in the surface pressure. These changes can be monitored when the
film undergoing photolysis is under pressure. No change in surface
pressure was observed after approximately 3.5 min. of photolysis,
therefore the duration of all photolyses was 5 min.

To create 100x co-area expanded films that contained enough
material that could be recovered and analyzed, the following
technique was utilized. After a 100x co-area film was formed, it
was photolyzed for 5 min and then it was compressed to
approximately 3 times its co-area with a teflon block. A new 100x
co-area film was spread between the block and the barrier and it
too was photolyzed. The teflon block was then removed (allowing
mixing of the two films) before the combined film was compressed to
approximately 3x co-area. This process was repeated two more times
and the combined films were recovered and analyzed.
II.2.4.2. Film Recovery Procedures

A 500 mL filter flask with a long piece of teflon (HPLC solvent delivery) tubing (1/8 in. I.D.) attached to it, is used as the aspirator trap. The trap and tubing were "acid-washed" prior to use (see above). The aspirator trap was attached to the water aspirator in the PML and a "lead donut" (I'RI Cheltenham, PA) was placed at its base to compensate for the weight of the vacuum hose. The balance lid was opened and the tip of the teflon tubing was used to aspirate the fully compressed film. The barrier was periodically moved to reduce the area available to the film, thus compensating for the material removed, and maintaining a high surface pressure. After the entire film had been removed (indicated by a very small area and no significant surface pressure), three 3 mL aliquots of HPLC-grade Hexanes were slowly dripped onto the tip of the teflon tubing, being aspirated into it and thoroughly rinsing it. This ensured that no film forming material remained inside the tubing. The contents of the trap were placed in an "acid-washed" separatory funnel where the aqueous phase was removed from the organic and extracted once more with hexanes. The combined hexane phases were dried over Na₂SO₄, and evaporated under vacuum in an "acid-washed" flask. Small amounts of CH₂Cl₂ were then used to wash the flask and were placed in an "acid-washed" sample vial where they were evaporated under vacuum.
II.2.4.3. Analysis by GC and GC-IR

Prior to GC analysis, the recovered material was transferred from the sample vial to a 0.1 mL conical vial using four 10 µL portions of hexane. The total volume in the conical vial was adjusted to 40 µL for most samples. Samples of very expanded photolyzed films required less solvent due to the lesser amount of material present.

A Hewlett-Packard Model 5890A Gas Chromatograph (GC) was used to obtain the gas chromatograms. A flame ionization detector was utilized with helium as the carrier gas. The injector temp. was set to 250°C and the detector temp. to 300°C. The capillary GC column used for the analyses was made of fused silica having a 0.53 mm internal diameter, a length of 10 m, and a bonded liquid stationary phase 1.2 µm thick (Alltech Associates, Inc., Deerfield, IL). The chemical composition of the liquid stationary phase (RSL-300) is polyphenylmethylsiloxane, equivalent to DB-17, HP-17, or OV-17. This column was used isothermally at 170°C with a carrier gas flow of 15 mL/min. A Hamilton 10 µL volumetric syringe was used for the GC injections, the typical injection consisting of approximately 1 µL. A Hamilton 1 µL syringe was used for injections of less than 1 µL.

Gas Chromatographic analysis in tandem with Infrared spectroscopy (GC-IR) were used in hopes of providing an unambiguous analysis of the GC peaks. In this technique, part of the GC
effluent (argon carrier gas) is diverted before it can be analyzed by the FID and directed onto a slowly rotating, cryogenic, gold-plated, cylindrical surface. The argon freezes when it encounters the cold surface and forms a matrix which traps any molecules that are present in the effluent. The parts of the frozen matrix containing the material represented by the GC peaks are then analyzed by IR spectroscopy. The Kratos GC used for these experiments was operated isothermally at 200°C, with a non-polar (DB5) capillary column. It provided chromatograms very similar to those obtained using the semi-polar RSL-300 capillary column.

II.3. Results

II.3.1. Isotherms and Creep Tests

Both of the two 1-diazo-2-oxoalkanoates (DOA) used in this study form high quality Langmuir films which reach a solid phase at a lower surface pressure than that required for the homologous carboxylic acids (vide infra). The transition point for DOH (Figure II.3.1) is at 15.5 dyn/cm, while that for DON (Figure II.3.2) is at 16.5 dyn/cm. The \( \pi/A \) isotherm curves of the two DOA molecules are very similar, both having liftoff areas of 21.2 \( A^\prime/molecule \) and identical co-areas of 19.6 \( A^\prime/molecule \). The difference between the two materials is in the collapse pressure of the film. DOH, having the short hydrophobic chain, collapses at 31 dyn/cm, while DON collapses at 49.8 dyn/cm. Similarly, the creep
Figure II.3.1. 1-Diazo-2-oxoheptadecane (DOH) \( \pi/A \) isotherm.

tests of DOH (Figure II.3.3) and DON films (Figure II.3.4) confirm that films formed from DOH are not as stable as those formed from DON.

The similar isotherm characteristics displayed by the films of these two materials contrast with the markedly different isotherm curve obtained from 1-diazo-2-oxopentadecanoate (DOP), reported by Holden and Ringsdorf\(^{24}\). Even though DOH has only one more methylene in its hydrophobic chain than DOP, it forms a much more stable film. In this regard, the film forming behavior of DOP and DOH mirror that of the analogous C\(_{15}\) and C\(_{16}\) acids.
Figure II.3.2. 1-Diazo-2-oxononadecane (DON) $\pi$/A isotherm.

Figure II.3.3. 1-Diazo-2-oxoheptadecane (DOH) creep test @ 2 dynes/cm.
Figure II.3.4. 1-Diazo-2-oxononadecane (DON) creep test @ 2 dyn/cm.

In order to better interpret the characteristics of the films that resulted from photolysis of DOA, we first studied films composed of the possible authentic monomeric photolysis products. These are 2-oxoheptadecanol (OHD) and heptadecanoic acid (C17 acid) from DOH photolysis, and 2-oxononadecanol (OND) and nonadecanoic acid (C19 acid) from DON.

Both the carboxylic acids and the α-hydroxy ketones (HK) formed excellent films. The isotherm curves of the carboxylic acids are in accord with those of the classic carboxylic acid isotherm. They each display a liftoff area of 23 Å²/molecule; C17
Figure II.3.5. Heptadecanoic ($C_{17}$) acid $\pi/A$ isotherm.

Figure II.3.6. Nonadecanoic ($C_{19}$) acid $\pi/A$ isotherm.
Figure II.3.7. Heptadecanoic ($\text{C}_{17}$) acid creep test @ 2 dyn/cm.

acid has a co-area of 19.3 $\text{A}^2$/molecule (Figure II.3.5), while $\text{C}_{19}$ acid has a co-area of 19.6 $\text{A}^2$/molecule (Figure II.3.6). The $\text{C}_{17}$ acid $\pi$/A isotherm displays a transition point at 23 dynes/cm and a collapse pressure around 49.5 dyn/cm. The $\text{C}_{19}$ acid $\pi$/A isotherm displays a transition point at 24.5 dyn/cm and the film collapses at 52 dyn/cm. The $\text{C}_{17}$ acid (Figure II.3.7) (possessing the shorter hydrophobic chain) creeped at a higher rate than $\text{C}_{19}$ acid (Figure II.3.8).

The shape of the $\pi$/A isotherm curves of the HKs are very different from those of the acids. They rise from the baseline...
Figure II.3.8. Nonadecanoic (C₁₉) acid creep test @ 2 dyn/cm.

Figure II.3.9. 2-Oxoheptadecanol (OHD) \(\pi/A\) isotherm.
Figure II.3.10. 2-Oxononadecanol (OND) $\pi$/A isotherm.

with a very steep slope (indicative of a solid phase), displaying no transition from a liquid phase. The $\pi$/A isotherm curve for OHD displays a liftoff area of 18.5 $\AA^2$/molecule, a co-area of 18.2 $\AA^2$/molecule and a high collapse pressure (59.8 dyn/cm, Figure II.3.9). The $\pi$/A isotherm curve for OND displays a liftoff area of 21 $\AA^2$/molecule, a co-area of 20.8 $\AA^2$/molecule and a collapse pressure of 60 dyn/cm (Figure II.3.10). The creep tests for the HK films are also very different from those of the acids (Figures II.3.11 and II.3.12). Even at the high constant pressure of 30 dynes/cm, an OND film shows almost no creep (Figure II.3.13).
Figure II.3.11. 2-Oxoheptadecanol (OHD) creep test @ 2 dyn/cm.

Figure II.3.12. 2-Oxononadecanol (OND) creep test @ 2 dyn/cm.
Figure II.3.13. 2-Oxononadecanol (OND) creep test @ 30 dyn/cm.

The π/A isotherms resulting from the photolyses of DOA films did not resemble that obtained from the HK nor that from the acid, but was rather intermediate between the two. The transition point occurred at a surface pressure lower than that observed for the acid, but was visible, unlike that of the HK. The π/A isotherm of a DON film which was photolyzed after it was compressed to 2 dyn/cm (Figure II.3.14) has a liftoff area of 20.5 Å²/molecule, a co-area of 19 Å²/molecule, a transition point at 13 dyn/cm and a collapse pressure of 52 dyn/cm. It is very similar to the π/A isotherm obtained from a DON film which was photolyzed while expanded at 4x
Figure II.3.14. DON film photolyzed while compressed at 2 dyn/cm $\pi$/$A$ isotherm.

Figure II.3.15. DON film photolyzed expanded (4x co-area) $\pi$/$A$ isotherm.
Figure II.3.16. DON film photolyzed while expanded (4x co-area) creep test @ 2 dyn/cm.

co-area (Figure II.3.15) which displays a liftoff of 21 A²/molecule, a co-area of 19 A²/molecule, a transition point at 15 dyn/cm, and collapses at 53.5 dyn/cm. The creep tests both at 2 (Figure II.3.16) and 30 (Figure II.3.17) dyn/cm constant pressure indicate that both of these photolyzed DON films were very stable.

Since it was possible that both the HK and the acid were being formed in a given photolysis, we studied mixed films of the two possible products. Solutions containing various ratios of HK and acid were prepared and the resulting isotherms were compared to those obtained from photolysis of DOA films. The solution containing 25% OND : 75% C₆ ACID gave a π/Å isotherm (Figure
Figure II.3.17. DON film photolyzed while compressed at 2 dyn/cm creep test @ 30 dyn/cm.

Figure II.3.18. 25% ODN:75% C18 acid (premixed) film $\pi$/A isotherm.
Figure II.3.19. 25% OND:75% C₁₉ acid (premixed) film creep test @ 2 dyn/cm.

II.3.18) that closely matched the one obtained from a photolyzed DON film. It displayed a liftoff area of 22 Å²/molecule, a co-area of 19 Å²/molecule, a transition point at 14 dyn/cm and a collapse pressure of 55.5 dyn/cm. The creep test of the mixed film (Figure II.3.19) was similar to those of the photolyzed DON films, showing very little creep, and indicating that a stable film formed.

The mixed films described above were prepared by spreading a single solution containing both the HK and the acid dissolved in it and were termed premixed. Another type of mixed film can be formed if two solutions, each containing either HK or acid, are spread on
Figure II.3.20. 20% OND:80% C₁₉ acid (non premixed) film π/A isotherm.

Figure II.3.21. 17% OND:83% C₁₉ acid (non premixed) film creep test @ 2 dyn/cm.
the water surface separately (non-premixed). The π/A isotherm curves of non-premixed films all looked the same, regardless of the relative amounts of HK and acid present. They had a liftoff area of 22.5 and a co-area of 19.6 Å²/molecule (Figure II.3.20). All displayed a sharp transition point at around 24 dyn/cm and collapsed at approximately 52 dyn/cm. Their creep tests showed these films to be more stable than the pure acid, but less stable than the pure HK film (Figure II.3.21).

It is also interesting to compare the post-film collapse behavior of the photolyzed DON film to that of the mixed OND/C₆₆ acid film. The photolyzed film was so rigid that it overflowed the lip of the trough when it was collapsed and rapidly compressed. This behavior was not seen for the mixed acid/HK films. Also, white "threads" were observed in collapsed films of photolyzed DON monolayers. These are attributed to defects where the monolayer collapses and "ridges", visible to the naked eye, are formed (analogous to the formation of mountain ranges from the action of tectonic plates). Such behavior is generally observed with very rigid films, and was never observed with mixed monolayers of C₆₆ acid and OND.

II.3.2. Viscosimetry Results

All viscosimeter canals used in these experiments were smooth and either 1/2 or 3/4 inch long. Since all three canal widths are
large, on a molecular scale, they should exert an effect only on assemblies that exhibit a substantial surface shear viscosity (viscosity). The three widths were, however, useful in studying various aspects of film behavior. In particular, the narrower slits enabled measurements of lower viscosities to be made.

It was found that there is a tremendous difference between the viscosity of photolyzed DON films and those of unphotolyzed DON, G₃ acid and OND and their mixtures. Furthermore, the viscosities of the photolyzed DON monolayers vary depending on the area that was available to the individual DON molecules during the irradiation. More specifically, we observed the following.

The results of the 1/8 inch canal viscosimetry (Figure II.3.22) showed that the DON films that were photolyzed compressed at 30 and 2 dyn/cm display the same viscosity (only the results of the film that was photolyzed at 2 dyn/cm are shown). The film with the next lowest viscosity is that obtained from DON photolyzed expanded at 4x co-area. and the lowest viscosity found for a photolyzed DON film was at 30x co-area. The viscosities of both of the non-compressed films were lower than that of the films that were photolyzed compressed.

Using the 1/16 inch canal viscosimeter, there was still no meaningful measure of viscosity in either films of unphotolyzed DON, or of the G₃ acid. Their viscosimetry curves coincide and only that of unphotolyzed DON is shown in Figure II.3.23. These
Figure II.3.22. Viscosimetry results using the 1/8 inch canal viscosimeter.

results do offer some evidence that the OND film is a little more viscous than those formed from C₆, ACID or unphotolyzed DON. The viscosity of the OND film however, is much lower than that of the photolyzed DON films. The viscosimetry results indicate that DON photolyzed expanded at 4x co-area and photolyzed compressed at 2 dyn/cm films, have the highest viscosity and their values are comparable. This is in direct contrast to measurements with the 1/8 inch canal viscosimeter which showed that the DON film that was photolyzed expanded at 4x co-area was less viscous than the DON film that was photolyzed compressed at 2 dyn/cm. Interestingly,
Figure II.3.23. Viscosimetry results using the 1/16 inch canal viscosimeter.

Figure II.3.24. Viscosimetry results using the 1/32 inch canal viscosimeter.
Table II.3.1. Summary of $\pi/A$ isotherm, creep test and viscosity measurement data.

<table>
<thead>
<tr>
<th>Condition</th>
<th>$\pi/A$ Isotherm</th>
<th>Creep</th>
<th>Viscosimetry</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Lift-off area A²/molecule</td>
<td>Trans. Coll. pt</td>
<td>$\pi$ init. mol. area</td>
</tr>
<tr>
<td>DOH</td>
<td>21.2</td>
<td>19.6</td>
<td>15.0</td>
</tr>
<tr>
<td>OHD</td>
<td>18.5</td>
<td>18.2</td>
<td>-</td>
</tr>
<tr>
<td>C₁₇ acid</td>
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<td>19.3</td>
<td>23.0</td>
</tr>
<tr>
<td>DON</td>
<td>21.2</td>
<td>19.6</td>
<td>15.2</td>
</tr>
<tr>
<td>OND</td>
<td>21.0</td>
<td>20.8</td>
<td>-</td>
</tr>
<tr>
<td>C₁₈ acid 25:75</td>
<td>23.2</td>
<td>19.6</td>
<td>24.6</td>
</tr>
<tr>
<td>OND:C₁₈ acid (premixed) 50:50</td>
<td>21.9</td>
<td>19.8</td>
<td>13.7</td>
</tr>
<tr>
<td>OND:C₁₈ acid (premixed) 20:80</td>
<td>20.5</td>
<td>19.5</td>
<td>6.6</td>
</tr>
<tr>
<td>OND:C₁₈ acid (non-premix) 40:60</td>
<td>22.3</td>
<td>19.6</td>
<td>24.1</td>
</tr>
<tr>
<td>OND:C₁₈ acid (non-premix) 40:60</td>
<td>21.7</td>
<td>19.7</td>
<td>24.2</td>
</tr>
<tr>
<td>DON UV/exp 100x co-area</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>DON UV/exp 30x co-area</td>
<td>22.1</td>
<td>18.8</td>
<td>13.2</td>
</tr>
<tr>
<td>DON UV/exp 4x co-area</td>
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<td>19.2</td>
<td>15.1</td>
</tr>
<tr>
<td>DON UV/comp 2 dyn/cm</td>
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<td>18.9</td>
<td>13.3</td>
</tr>
<tr>
<td>DON UV/comp 30 dyn/cm</td>
<td>21.3</td>
<td>19.3</td>
<td>13.5</td>
</tr>
</tbody>
</table>

* denotes a creep test result at a constant pressure of 30 dyn/cm
the viscosity displayed by the DON films that were photolyzed compressed at 30 dyn/cm is lower than that of the 2 dyn/cm compressed or the 4x co-area expanded film. The DON films that were photolyzed expanded at 30x and 100x co-area display the lowest viscosity among the photolyzed films. They are, however, still more viscous than the unphotolyzed DON, C₁₃ acid and even the OND monolayers.

The 1/32 inch canal viscosimetry measurement results (Figure II.3.24) mirror the trends observed for the 1/16 inch measurements. The OND film has a higher viscosity than the unphotolyzed DON film. The viscosities of the DON films that were photolyzed compressed at 2 dyn/cm and expanded at 4x co-area are similar under these measurement conditions as well, although the film that was photolyzed expanded seems to be a little more viscous. All of the results of the π/A isotherms and creep tests are summarized in Table II.3.1. Viscosity measurement data are also included in this table.

Various data representations and analyses ("spectra") can be obtained using the surface shear viscosity determination computer package. The following examples were obtained from a DON film which was photolyzed at a surface pressure of 2 dynes/cm. The π/A isotherm data give rise to the kₚ/π (elastic modulus/surface pressure) plot (Figure II.3.25). The π/t data derived from the
viscosimetry experiments and give rise to the $\frac{dx}{dt}$ plot (Figure II.3.26). A combination of the above produced the $/\pi$ (surface shear viscosity/surface pressure) plot (Figure II.3.27).

The first experiments using this methodology for determining surface shear viscosity have provided interesting data. However, the method needs refinement in several ways in order to achieve results independent of canal width for Newtonian monomolecular films. The purpose here was to explore the possibility of using viscosity "spectra" to understand structural details and transformations as a function of surface pressure in the Langmuir
Figure II.3.26. Derivative of surface pressure over time vs surface pressure plot.

Figure II.3.27. Surface shear viscosity vs surface pressure plot.
film. The results obtained from this method are semi quantitative. The shapes of the spectra are more reliable than the magnitude of the viscosity coefficients, although the coefficients are of the right order of magnitude.

We are planning to use this methodology to study films of materials that have a well defined viscosity (their viscosity has been determined using the traditional method). The results from this study can then lead to a quantitation of the surface shear viscosity values that we obtain.

II.3.3. GC and GC-IR Results

GC can be useful for the analysis of the materials obtained from the photolysis of the DON film at the air/water interface because of the sensitivity of the FID. It was used to analyze recovered films of authentic DON, C18 acid and OND samples, as well as photolyzed DON films. However, using GC for the analysis introduces some drawbacks. Dimeric, or oligomeric photolysis products of our long chain compounds will in general not be observed. The best one could hope to achieve is to measure the amount of unreacted DON, as well as the ratio of acid to HK products.

We found that DON decomposes under the GC conditions employed, as evidenced by the fact that multiple peaks (retention times of 4.0, 6.6, 9.5 and 11.4 min) are observed when it is injected alone,
even when the column temp. is reduced to 140°C. Diazot compounds are known to be heat sensitive and DON is probably undergoing thermolysis in the injector. GC-IR analysis of these peaks indicated the presence of ketene (in the peak with the shortest retention time, absorption at 2126 cm\(^{-1}\)), and various types of carbonyls (in the other three peaks). No evidence of the diazo group (2106 cm\(^{-1}\)) was found in any of these peaks.

Our hope of using the GC analysis to determine the ratio of monomeric photolysis products was not realized either. Injection of pure C\(_9\), acid caused the appearance of a peak with a retention time of 13.5 min., while injection of pure OND caused the appearance of a peak with a retention time of 16.6 min. These peaks were baseline separated. GC-IR analysis proved that the peaks resulting from injections of the pure acid or HK indeed were composed of these materials. In solution IR spectra of mixtures of OND and C\(_9\), acid, the carbonyl absorptions cannot be differentiated, since they appear only 11 cm\(^{-1}\) apart from each other. The C\(_9\), acid forms dimers in solution,\(^{43}\) decreasing the frequency of its carbonyl absorption. In GC-IR spectra of mixtures however, the carbonyl absorptions are easily differentiated, being 60 cm\(^{-1}\) apart, because the C\(_9\), acid is trapped in a monomeric form.

GC-IR analysis of acid/HK mixtures indicated that these compounds do not emerge from the GC column as separate peaks, but that complexation of some type is occurring. Mixtures of the two
compounds were shown to be present in a single peak. More specifically, when a 1:2 ratio of acid:HK was injected, a single peak containing both compounds appeared, possessing a retention time intermediate between those of the acid and HK. When a 2:1 ratio of acid:HK was injected, two peaks possessing the retention times of the acid and HK appeared. The peak with the retention time of the acid contained only acid, while the other contained a mixture of both materials.

It is because of the observed complexation of acid and HK that quantitative GC results were not obtained. The following qualitative results can be reported for the GC analyses of recovered, photolyzed DON films. All the chromatograms displayed a substantial peak with a retention time similar to that of C₉ acid. This confirms the report by Ringsdorf and Holden. Small peaks were always present with retention times similar to those of the DON degradation products, indicating some unreacted starting material remained. No peak with a retention time similar to OND was observed in any of the recovered films that were photolyzed while expanded. The only films that displayed a very small peak with a retention time similar to OND were those that had been photolyzed compressed. The size of the peak with the retention time of OND was very small in comparison to that which appeared with the retention time of C₉ acid. The size of the peak with the retention time of OND was slightly larger in recovered DON films.
that had been photolyzed compressed at 30 dyn/cm than in those that had been photolyzed compressed at 2 dyn/cm.

II.4. Discussion
II.4.1. Monomeric Films Composed of Acid or Unphotolyzed DOA

The films produced from C\textsubscript{17} and C\textsubscript{19} acids are typical of long chain carboxylic acids. The π/A isotherms of both materials have a liftoff area of approximately 23 Å\textsuperscript{2}/molecule which indicates the beginning of the liquid phase. The liquid phase continues to rather high pressure (23 dyn/cm for C\textsubscript{17} acid, 25 dyn/cm for C\textsubscript{19} acid) where a very sharp transition to the solid phase is observed. The co-areas for both materials are approximately 19.5 Å\textsuperscript{2}/molecule, which is the typical value observed in carboxylic acid π/A isotherms. The differences between the two materials include the observations that the slope of the π/A isotherm curve corresponding to the liquid phase is a little steeper for C\textsubscript{19} acid and the collapse pressure is higher for this material as well. This is the result of the longer hydrophobic chain in this material, which causes the film that it forms to be less compressible and maintain its integrity to a higher surface pressure than C\textsubscript{17} acid. The higher stability of the film formed from C\textsubscript{19} acid is also evident in its creep test, which does not creep as much as that of C\textsubscript{17} acid. The viscosity measurements were performed at 30 dyn/cm to ensure that even the acid films would be in the solid phase.
Nevertheless, the viscosity measurements indicate that films of both acids have a very low viscosity.

The films formed from DOH and DON are stable and well behaved. The π/A isotherms of both display a liftoff area of approximately 21 A²/molecule. The liquid phase begins at this point and ends at the transition point observed at 15 dyn/cm. The co-areas for both films are 19.6 A²/molecule. The two methylene difference in the hydrophobic chain of the two materials manifests itself in the higher collapse pressure and the more stable creep test behavior that is observed for DON. However, as seen for the acids, even the film of the longer chain compound shows a very low viscosity.

II.4.2. Monomeric Films Composed of Hydroxy Ketones (OHD and OMD)

The difference between HKs and their isomeric carboxylic acids is the presence of a methylene between the carbonyl and -OH groups. This difference in structure causes tremendous differences in the properties of the film that is formed. Perhaps the most striking of these properties is the total absence of any liquid phase in the π/A isotherm. The film is in the solid phase almost as soon as a surface pressure rise occurs. The very steep slope of the π/A isotherm curve combined with the high collapse pressure indicate that the film has a very low compressibility. Interestingly, the difference in the length of the hydrophobic chain does not cause a difference between the collapse pressures of the two HKs. The
creep test is another indicator of the very high stability of this film. The regular creep test at 2 dyn/cm shows no barrier movement, while a creep test at 30 dyn/cm (a rather high surface pressure), also causes almost no film creep. The high rigidity present in these films is also evident in their viscosity. Although monomeric, the HK displayed the highest viscosity of any non-photolyzed film that we studied. One possible explanation of this kind of film stability might be a hydrogen bond-based oligomerization of the sort shown in Figure II.4.1. Given the separate carbonyl and hydroxy groups, an extended network can be formed in this manner, linking an HK molecule to its neighbors in a two-dimensional array. Additional evidence bearing on such intermolecular interactions will be discussed in reference to HK/acid mixed films, below.
II.4.3. Films from Mixtures of Monomeric Materials

The films formed from mixtures of OHD and C17 acid and OND and C19 acid were more stable than those formed only from the acids. Two types of film were studied, those that were formed by spreading a single solution which contained both acid and HK (premixed) and those that were formed by depositing two different solutions, each containing either acid or HK (non premixed). The $\pi/A$ isotherms obtained from non premixed solutions all looked the same, regardless of the relative amounts of the two materials present. They displayed a lift-off area of approximately 22.3 $\text{Å}^2$/molecule and a transition point at around 24.3 dyn/cm, just like the films of their acid component. The films collapsed at approximately 52 dyn/cm and displayed co-areas of 19.6 $\text{Å}^2$/molecule. The creep tests were more stable than those of the acids, but less stable than those of the HKs. This behavior is consistent with island, or domain, formation where like molecules form small aggregates on the water surface. Since some of these aggregates are composed of acid molecules, they (initially) display their characteristic liquid phase behavior, while the others that are composed of the HK molecules are in the solid phase and have no effect on this particular phase.

The $\pi/A$ isotherms of the premixed films look different from those of the non premixed films because the transition point is not fixed at a given pressure, but varies depending on the film
composition. If more HK is present, the transition point pressure is lowered, while increasing the percentage of acid raises the transition point surface pressure. The liftoff area also varies depending on the magnitude of the transition point pressure. By increasing the relative amount of acid in the film, the liftoff area increases to appear more acid like. The collapse pressure, the co-area and the creep test stability of these films are the same as those of the non premixed films. From the above observations it can be suggested that the molecules in the premixed films do not form islands, but are well dispersed within the film. We are attempting to obtain independent confirmation for the island formation by fluorescence microscopy.

Additional evidence for the kinds of interactions that can occur between acids and HKs is obtained by an analysis of their IR spectra. Carboxylic acids form dimers in solution and the effects of dimer formation are evident in the liquid IR spectra of acids. The carbonyl stretching frequency of the dimeric carboxylic acids is usually from 30 to 60 cm\(^{-1}\) lower in frequency than that of the monomeric species. The C\(_{6}\) acid carbonyl absorption, observed at 1771 cm\(^{-1}\) in the matrix isolated GC-IR spectrum, is shifted to 1711 cm\(^{-1}\) in the liquid IR spectrum. The OND solution infrared spectrum differs only slightly from that obtained under GC-IR conditions. The carbonyl absorption at 1728 cm\(^{-1}\) appears at 1722 cm\(^{-1}\) in the solution IR spectrum. The slight decrease in the carbonyl
absorption could be an indication of self-association or solvation effects (such as inter- or intramolecular hydrogen bonding) in the liquid infrared spectrum.

An acid/HK complex is observed in the GC-IR analysis of mixed films and is suspected in the premixed films. It is likely due to a hydrogen bonding interaction similar to that which causes the self-association of the pure C₆₄ acid and OMD described above. The reason that a complex may be preferentially formed between an acid and a HK, rather than between like molecules is unclear. One hypothesis is that the acidic proton of the acid, being more available than its counterpart in the HK, is preferentially hydrogen bound by the HK carbonyl oxygen. This is not conjugated like in the acid and should form a stronger hydrogen bond.

II.4.4. Films from the Photolysis of DOA at the Air-Water Interface

Having shown that films of DOA are formed and that they are stable, we studied their photoreaction at the air/water interface. Since the reaction is initiated by UV irradiation, one of the photolytic reaction pathways will be followed, leading to either a carbene or a ketene. Acid-catalyzed decomposition of the DOA molecules by the subphase is not likely to occur, as the water has a pH value of approximately 5.5 and this is not acidic enough.
The 1-diazo-2-oxo functionality is the polar group of the molecule and as such it is in intimate contact with the water subphase. As soon as carbene is formed it can undergo insertion into a water molecule leading to an HK. If the carbene rearranges to the ketene, then reaction with a water molecule will give rise to an acid which will have one more methylene in its hydrocarbon chain than the parent DOA. Carbene may not have a chance to rearrange to the ketene if water molecules are readily accessible to it and/or the monolayer environment retards rearrangement to ketene. The product formed may indicate the type of contact that exists between this polar group and the subphase molecules, as well as how quickly the carbene to ketene rearrangement occurs.

While Ringsdorf and Holden reported exclusive formation of acid and ketene dimer, we expected product distribution differences based on the space that was available to a DOA molecule in the Langmuir film. The molecular area should dictate whether the molecule can attain a particular conformation, as well as its distance from its nearest neighbors, and its orientation at the interface. For this reason the photolyses were carried out at various surface pressures, i.e. various molecular areas.

When a photolysis occurs under compressed conditions, the film is in a liquid or solid state and a measurable surface pressure exists. The DON film is in the liquid state at a surface pressure of 2 dyn/cm and the molecules should display limited mobility.
The DON film has undergone a phase transition and is in the solid state at 30 dyn/cm; the molecules are expected to be constrained in a given conformation inside the tightly packed film with much less molecular motion allowed. In these film states the molecules are close to being perpendicular to the interface with the polar groups in close proximity to one another. If a carbene were to be formed in this type of configuration, the Wolff rearrangement might not occur as readily due to the steric hindrance imposed by the neighboring molecules. Thus, when a DOA film is photolyzed compressed, there might be a higher chance for carbene insertion into water leading to HK formation.

When a film undergoes photolysis in an expanded state no surface pressure exists, as the molecular area is larger than the liftoff area. However, expanded photolyses can be differentiated by comparing the area available per molecule. Expanded photolyses were carried out with the film expanded to multiples of the co-area: 4x, 30x and 100x. The molecules are still fairly close to each other at the 4x co-area expanded film, the hydrophobic tails being in contact, while the polar head groups are a little further separated than in the close packed film. The Wolff rearrangement might be expected to be somewhat more easily accomplished with the film in this state rather than in a compressed film. The 30x co-area expanded film is truly expanded. The area available for each molecule is such that it can lay on its side fully extended without
coming into contact with neighboring molecules. In the 100x co-area expanded film enough space is allowed per molecule so that there is only a small chance of any contact between neighboring molecules. This presumes that the monolayer behaves as a true gaseous film, with individual molecules tending to spread as far away from each other as possible on the interface, and that no molecular aggregates are being formed. If the above holds true and there are no steric constraints on the DOA molecule from its neighbors, the major product that is formed from the photolyses at 30x and 100x co-area will give us an indication of how well the carbene insertion into water competes with an unrestricted Wolff rearrangement.

All the photolyzed DON film π/A isotherms resembled that obtained from a 25% OND:75% C19 acid solution. The creep tests however indicated that photolyzed DON films were more stable than either the non-premixed or the premixed films. Specifically, the π/A isotherm of the photolyzed DON films all had liftoff areas between 20.7 and 22.1 and co-areas between 18.8 and 19.3 A²/molecule. Their transition points were 13.3±0.2, except for the film photolyzed at 4x which had a transition point of 15.1 dyn/cm. The collapse pressures increased as the area per molecule increased (48.3 for the film photolyzed while compressed at 30 dyn/cm to 55.0 for that photolyzed expanded at 30x co-area). None of the
photolyzed films crept more than 1.5% during 1 h of compression at 30 dyn/cm.

The x/A isotherm data of the photolyzed DON films are similar to those seen for a 25% OND:75% C₆₅ acid premixed film. The creep test data give indications that the photolyzed films are very stable. But the large difference in the viscosity of the photoreaction products from that of the expected monomeric products can be interpreted as an indication that dimeric or oligomeric products are formed. In order for dimeric or oligomeric products to be formed the carbene or ketene must react with other unphotolyzed or photolyzed DOA molecules instead of inserting into a water molecule. The possible reactions that could lead to these higher molecular weight products have already been discussed in II.1 and include among others ketene dimerization, ketene reaction with a carboxylic acid and carbene insertion into C-H or O-H bonds.

It appears that the films resulting from the photolysis of closely packed monolayers (compressed at 2 and 30 dyn/cm) are the most viscous films obtainable, as seen from the 1/8 inch viscosimetry results. The molecules are as close as possible to each other, most likely resulting in a film that displays the highest degree of crosslinking between neighboring molecules. The crosslinking probably takes place in, or in the area around, the polar head group. The close packing of the molecules might also be implicated in the observation of some HK formation. The 1/16 inch
viscosimetry results indicate that the film photolyzed at 2 dyn/cm is more viscous than that photolyzed at 30 dyn/cm. This could indicate that some extent of molecular motion is necessary in order to obtain the film with the highest degree of crosslinking.

The films resulting from 4x co-area expanded photolysis are only slightly less viscous than the compressed photolyzed films, as is indicated only from the 1/8 inch viscosimetry results. The 1/16 inch viscosimetry results indicate that these films' viscosity is comparable to that of the films photolyzed while compressed at 2 dyn/cm. The 1/32 inch viscosimetry results indicate that their viscosity is actually a little higher than that of the films photolyzed while compressed at 2 dyn/cm. The small increase in the area allotted to the polar head group in this configuration is probably not enough to cause a significant drop in the extent of crosslinking. Crosslinking is still expected to occur predominantly in the vicinity of the polar head group for these films. The reason for the apparent reversal in film viscosity order between these films and those obtained from the photolysis of films compressed at 30 and 2 dyn/cm in going from the 1/8 inch to the narrower canal widths is not immediately obvious. Perhaps the size, shape and flexibility of the crosslinked portions of these films are such that the narrower canal widths significantly inhibit them from flowing through the canal, while the 1/8 inch canal is just too wide for such an effect to be observed.
The lowest viscosity among the photolyzed DON films is exhibited by the films resulting from photolysis while expanded at 100x co-area. This film is somewhat less viscous than that formed from photolysis at 30x co-area. Even these extremely expanded films however formed products with a higher viscosity than the monomeric compounds upon photolysis. This indicates that the Langmuir film is still not in the gaseous state despite the truly large area available to each molecule. If islands are formed, the dimeric/oligomeric material is probably formed by carbene/ketene reaction with a portion of the head group. If, on the other hand, something approaching a film in a gaseous phase is formed, the viscous material that is produced may contain bonds created by carbene insertion into C-H bonds that are located in parts of the molecule other than the polar head group. Island formation could also be due to formation of aggregates in the CHCl, spreading solution of DON. The characteristics and the number of islands formed (their size should be fairly consistent) and how quickly they might dissipate back to a gaseous monolayer in the film, will likely determine the viscosity of the film. Product with a higher viscosity should be formed if the molecules comprising an island are crosslinked than if those in a monolayer in the gaseous state are crosslinked. The fact that these films display the lowest viscosity among the irradiated monolayers is an indication that the
molecules are definitely more spread out in these films, even though they may not be forming a gaseous monolayer.

II.4.5. Chromatographic Analysis of the Reaction Products

In an effort to augment the information obtained from our π/A isotherm, creep test and viscosity measurements, we attempted to chromatographically analyze the photolysis product mixture. HPLC separation conditions were already known and had been used for the purification of the HK and acid. A lower limit of detection (for either the DOA starting material or the HK and acid products) of 1 nanomole was needed for cases where a large amount of one product was present over the other, or a little of the unreacted starting material was recovered. Neither our RI (refractive index) detector (Waters 401), nor the more sensitive RI Waters 410 (coupled with a column heater to minimize baseline fluctuations) could meet these detection limits. The smallest amounts of material that could be detected with the better RI detector were 3 to 10 nmol (different materials have varying RI response). We therefore decided to explore alternative HPLC detection methods.

HPLC utilizing electrochemical detectors (LCEC) has a reputation for being very sensitive," so we explored whether this method could provide us with the desired sensitivity. Cyclic voltammograms (CV) of our compounds exhibited a redox potential (albeit a weak one), therefore we were confident that they could be
detected using LCEC. A requirement for an electrochemical cell is that an electrolyte must be present, and in the case of LCEC it must be soluble in the mobile phase used. Tetraethylammonium perchlorate (TEAP) is an electrolyte that is soluble in the methanolic mobile phase that we were using and was utilized for all LCEC experiments. However, both an older LCEC setup (Dr. Harik's laboratories, Neurology Department, University Hospitals of Cleveland) and a state of the art LCEC detector (Model 400, EG&G, Princeton Applied Research) were incapable of providing us with the sensitivity we needed. The lowest amounts of material that could be detected with the better LCEC were 40-60 nmol. Due to the flame ionization detector (FID) present in many gas chromatographs, a much smaller amount of material can be detected than by an HPLC detector. The disadvantage associated with this method is that the sample must be vaporized. The higher the molecular weight of the compound, the higher the temperature required to vaporize it. This places a constraint on the size of the species that can be studied by GC. We had hesitated to consider GC as an appropriate separation method because of the rather large size of the molecules we were interested in separating. However, we found that, as opposed to regular packed-column GC, capillary-column GC was capable of separating our high molecular weight, long chain DOA, as well as the HK and acid products that can result from its photoreaction. The elution times were fairly short and the
sensitivity was much more than we required. Capillary GC columns are composed of a fused silica capillary tube that is coated with a viscous liquid phase on the inside. The molecules undergoing chromatographic separation interact with the liquid phase at the liquid gas interface, providing shorter elution times than would be obtained by using a packed GC column. After identifying the best separation conditions we set forth to analyze the products of a photolysis at the gas-water interface.

In order to ensure that we were not preferentially recovering one possible product over another, we conducted recovery experiments of mixed films, where known amounts of each material were present in the film. We found that efficient recovery of carboxylic acids required that all apparatus that came in contact with the recovered film be washed with a dilute acid solution.

Upon injection of the recovered photolyzed DON films, the major product peak observed was attributed to the C₉ acid. A very small peak (at least two orders of magnitude smaller than the acid peak) attributed to OND was also observed, along with small peaks attributable to the degradation products of unreacted DON. However, since GC-IR showed that C₉ acid is complexed and co-elutes with OND, it is difficult to quantify their relative amounts. Overall, the integration of the observed peaks correlated to amounts of material that were significantly smaller than those expected, based on the efficiency of recovery of films of known
composition. Monitoring the GC column effluent well past the elution time of the last expected peak did not give any indications of longer retention time products (the expected higher molecular weight products) being present.

II.5. Conclusions

We have confirmed that the photolysis of DOA molecules in Langmuir films gives extensive Wolff rearrangement. The steric limitations that are likely placed on individual molecules by the surrounding organized film matrix do produce some of the non-rearranged water insertion product (HK), albeit a very small amount. More importantly, we have found that higher molecular weight products (dimers/oligomers) are formed regardless of how much space is available to the individual molecules. The extent of crosslinking between molecules is surface pressure dependent as can be seen from our viscosity measurements. Clearly the Ringsdorf, Holden picture of only acid and ketene dimer in a constant ratio is an oversimplification of this system. More work, possibly with SFC/FID, is needed to better assay the photolysis products.
Chapter III. Structure and Reactions in [22.3.3]Propellane Monolayers

III.1. Introduction

III.1.1. Propellane Characteristics

Various aspects of propellanes have been studied by our research group. [m.3.3]propellanes have been used as probes for ordered binding in solution aggregates. Single-crystal structures of the [12.3.3]propellane dione and syn,syn diol have been reported. More structural information obtained from NMR and C6H6-CIMS studies for an array of [m.3.3]propellane diones, ketols, and diols (m = 3, 4, 10, 12, 22) has also been reported (Figure III.1.1).

In the present study we wanted to investigate whether propellanes would form monolayers at the air-water interface, and if they did, to elucidate their orientation and their reactions. We were prompted to investigate the behavior of these molecules in monolayers by the observation that they exhibited a preferential orientation in aqueous micelles and vesicles. In these assemblies the large ring is aligned radially within the aggregate and the two smaller, oxygen containing rings, are held tangential to the aggregate surface (Figure III.1.2). Only the larger (m = 10, 12, 22) propellanes could be envisioned as candidates, since the large polymethylene ring is necessary to serve as the hydrophobic portion.
Figure III.1.1. Propellane dione and its reduction products.

of the amphiphilic molecule. The hydrophilic portion of the molecule would then be composed of the carbonyl and/or hydroxyl groups located at the apices of the small rings of the propellanes (Figure III.1.3).
Figure III.1.2. Propellane binding in micelles and vesicles.

The questions to be addressed for propellane monolayers were whether the two carbonyl and/or hydroxyl groups could exhibit enough of a polar influence to orient the molecules, and also how
Figure III.1.3. Expected propellane dione orientation at the air/water interface.

these molecules would fill space in the plane of the monolayer.
The molecules which traditionally form high quality Langmuir films have a distinctly cylindrical shape (e.g. long-chain fatty acids or alcohols), or have components which have a cylindrical shape (e.g. phospholipids). The propellanes on the other hand, have a distinctly non-cylindrical shape which, it could be argued, might not be able to pack well in a monolayer and would lead to unstable Langmuir films.

We have shown that propellane diones, ketols, and diols all form ordered, stable Langmuir films.\textsuperscript{44} These films have been characterized by their isotherms, as well as by their creep tests. The fact that stable films are formed, suggests that the propellane molecules accomplish efficient filling of space in the monolayer. This could lead to a better understanding of how unusually shaped molecules efficiently fill space when constrained at the air/water interface.
III.1.2 Propellane Reductions in Organized Assemblies

The sodium borohydride (BH₄⁻) reduction of propellanes in methanol, water, and in the presence of micelles, reverse micelles, and vesicles has been well studied. Experiments performed using the water soluble [4.3.3] and [10.3.3]propellanes indicated that the same product distribution is obtained whether the reduction occurs in methanol or in water with added tetramethylammonium bromide (TMABr) or trimethylamine oxide (TMAO). Thus, performing the reduction in methanol yields results equivalent to those expected for the bulk water reduction. It has been shown that when the reduction occurs in the presence of micellar assemblies, the ratio of products formed is different from that observed for the bulk reduction. Due to the specific orientation in which the propellanes are bound in these assemblies, the stereoselectivity of the direction of attack of the reducing agent depended on the reaction conditions. The reduction of [22.3.3]propellane anti ketol can give rise to two possible diols, anti,anti diol (a,a diol) and syn,anti diol (s,a diol) (Figure III.1.1). The a,a diol formation will be used to illustrate the differences in product distribution which arise from the specific reaction environment where the reduction is occurring. In the bulk solution, BH₄⁻ attack on [22.3.3]propellane anti ketol gives rise to 70% a,a diol (Table III.1.1). The reduction in a cationic micelle raises the amount of a,a diol formed to 86%. The propellane is
Table III.1.1. NaBH₄ reduction of [22.3.3]propellane anti ketol.

<table>
<thead>
<tr>
<th>Reduction environment</th>
<th>% a,a diol</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeOH (bulk)</td>
<td>70</td>
</tr>
<tr>
<td>CTABr micelles</td>
<td>86</td>
</tr>
<tr>
<td>DDABr reverse micelles</td>
<td>47</td>
</tr>
</tbody>
</table>

bound to the micelle in such an orientation that the polymethylene ring is directed radially towards the micelle center and the bicyclooctane base resides between the Stern layer and the aqueous environment (Figure III.1.2). In this type of aggregate the BH₄⁻ is located in the Stern layer and attacks the ketone functionality of the anti ketol from the direction of the polymethylene ring resulting in formation of a higher percentage of a,a diol than in the bulk reduction. In reverse micelles the BH₄⁻ is located in the water pool in the middle of the micelle, while the propellane is located mostly in the organic phase (benzene) and in the hydrophobic part of the reverse micelle. Reduction in this type of aggregates indicates a slight preference for the formation of the diol resulting from BH₄⁻ attack from the side of the bicyclooctane propellane base opposite the hydrophobic ring.

We decided to study the BH₄⁻ reduction of [22.3.3]propellane anti ketol constrained in monolayer films at the air/water
interface. The ratio of the diol products formed, when compared to
those obtained from the reduction in other types of organized
media, can provide information about the effect of the increased
molecular organization in the film on the stereoselectivity of the
reduction. A method sensitive enough to be used with the very
small quantities of material present in a Langmuir film is
necessary in order to quantitate the results of the reduction.
Radioactive labelling of the anti ketol propellane, separation of
the reduction products, and counting of the radioactivity would
provide us with a quantitation technique that is very sensitive.
The radioactive label present in the starting material would have
to remain present in the products however, for this technique to be
effective. Acid catalyzed labelling of a [20.3.3]propellane dione
with tritium (H) has been reported. The authors reported that
the hydrogens α- to the carbonyl groups were exchanged with tritium
atoms by heating the material in the presence of tritiated water in
a strongly acidic environment. An equivalent result was obtained
when we heated [22.3.3]propellane anti ketol in the presence of
tritiated water in a strongly basic environment. Since the protons
α- to the carbonyl group are exchanged with tritium atoms, the
label will become permanently incorporated into the molecule after
the carbonyl group is reduced to an alcohol.
III.2. Experimental

The experimental details of monolayer formation and analysis have already been described in chapter II, section 2. Those that were only utilized in conjunction with propellane monolayers are described here.

III.2.1. Surfactant Synthesis and Purification

The synthesis of the various [22.3.3]propellane molecules has already been described. All propellane preparations include chromatographic separation of the product mixtures formed. The fractions collected from the preparative HPLC separation were subjected to analytical HPLC and no contaminants were found. They were used with no further purification.

III.2.1.1. ³H-Labelled [22.3.3]Propellane-26-keto-29-anti-ol

[22.3.3]propellane-26-keto-29-anti-ol (3 mg, 6.66 μmol) was transferred into a tared 2 mL conical vial with a glass rod (owing to the viscous liquid consistency of the material). THF (400 μL dry, freshly distilled), a small piece of NaOH pellet (approx. 25 mg) and 20 μL tritiated water (50 mCi/mL) were added and the vial was sealed with a screw-cap containing a teflon-backed rubber septum. Upon shaking, the solution became homogeneous. The lower part of the vial was placed in a heating block at 50°C and the solution was heated for 24 h.
The reaction vial was then placed in the apparatus depicted in Figure III.2.1. All vials are borosilicate glass and possess screw caps with teflon-coated rubber septa. All tubing and cartridges are made of teflon. The silica, MgSO₄ and P₂O₅ were previously unused materials, having been rinsed thoroughly with CH₂Cl₂ (along with the rest of the apparatus) before use. A dry N₂ flow forced the solution through a NaOH trap/drying tube (silica/MgSO₄) into the collection vial. The collection vial was heated at 50°C, causing the solvent to evaporate and leaving the ℎ-labelled material. The solvent was trapped by the condenser which was kept in a dry ice/acetone bath. After the THF had evaporated, the reaction vial was rinsed with 500 μL CH₂Cl₂, which was injected
through the septum. This too was carried to the collection vial by the \( N_2 \) flow. After the collection vial was dry, the rinse was repeated two more times.

The \(^3\)H-labelled material was purified by analytical HPLC. A regular phase (Si) Rainin Dynamax column was used with a mobile phase consisting of 85% hexane, 10% ethyl acetate (EtOAc), 5% Isopropanol (iPr), at a flow of 1.5 \( \text{mL/min} \). The retention time was 5.5 min. The HPLC eluent was placed in a 2 \( \text{mL} \) volumetric test tube, where it was concentrated to dryness under a gentle \( N_2 \) flow. 1.9 mg of colorless, oily liquid were recovered; yield 63%.

Material was dissolved into 2 \( \text{mL} \) CHCl\(_3\). An 8 \( \mu\text{L} \) sample was assayed for tritium and showed 52,233 dpm (disintegrations per minute) from which the activity of the solution is calculated to be 2.9 \( \mu\text{Ci/mL} \) (1 \( \mu\text{Ci} = 2.22 \times 10^4 \) dpm). Since the \(^3\)H-labelled material had been collected following analytical HPLC separation, no further purification was performed.

III.2.2. Monolayer Formation

III.2.2.1. Clean Room

III.2.2.1.a. The Subphase

In experiments requiring a saturated NaCl subphase, the PML-purified water was added to a 1-L volumetric flask containing >350g of NaCl (Fisher, Certified ACS) and mixed by brisk shaking, until no further dissolution of NaCl could be detected. A large amount
of NaCl is needed to saturate a liter of water. Despite obtaining Certified ACS grade NaCl, the amount needed made it impossible to avoid having surface-active impurities present. To compensate, the following cycle was repeated as many times as it was necessary to bring the surface pressure down to 1.0-1.5 dyn/cm after the movable barrier was fully compressed (this residual surface pressure could not be eliminated). The surface of the subphase was "swept" with the movable barrier and an aspirator was used to remove whatever surface-active impurities had accumulated between the movable barrier and the pressure transducer at their closest proximity, the barrier was expanded fully, allowed to stand for 45 min. and the cycle was repeated.

In order to perform the sodium borohydride reductions of the anti-ketol propellane, the pH of the subphase had to be adjusted to be slightly basic so that the NaBH₄ would not be destroyed. To do this, 5 mL of a 1M NaOH and 2M NaBH₄ solution were spread behind the movable barrier. By allowing the system to equilibrate over approximately 2 h the subphase pH stabilized at 8 and any surface active impurities that might be present in the solution were trapped behind the barrier and could not interfere with the film. The balance surface was swept and aspirated immediately before spreading the film, to be sure that no surface active impurities were present.
III.2.2.1.b. Glassware cleanliness

The aspirator trap and teflon tubing used for the recovery of the films and all glassware used to extract the recovered material from the aqueous phase were rinsed repeatedly with CH₂Cl₂, followed by acetone.

III.2.2.1.c. Compound Solutions

The solutions of non-radioactively labelled compounds were prepared in Class A, Pyrex, 25 mL volumetric flasks, which were standard degreased, as described in II.2.4.1.e. Solutions were formed by dissolving 6.5-11.3 mg of compound in CH₂Cl₂. The radioactively labelled anti-ketol propellane solution was prepared in a Pyrex, 2 mL volumetric test tube which had been standard degreased and carried to the chemistry laboratory in a Class-100 bag. A teflon stopper was used. The concentration of the resulting solution (for the radioactively labelled material) was not very accurate, as the weight of the material was determined by weighing by difference, after the HPLC mobile phase was evaporated under a slow N₂ stream.

III.2.2.2. Procedure for Film Formation

For non-radioactively labelled propellane films, a 60-80 μL sample of the surfactant solution was spread on the subphase and the solvent allowed to evaporate. The film was then slowly
compressed at 2 Å/molecule/min using the movable barrier as described in II.2.4.2. For radioactively labelled films, a 4-50 μL sample of the solution was spread on the subphase using a 50 μL volumetric syringe (Hamilton) and the solvent was allowed to evaporate. If an expanded film was studied, the monolayer was considered in contact with the subphase as soon as the solvent evaporated, for length of reaction timekeeping purposes. To create compressed films, the monolayer was compressed at approximately 5 Å/molecule/minute as soon as the solvent had evaporated. The automatic pressure control (preset to desired surface pressure) was engaged when a pressure increase was observed. Length of reaction timekeeping began after the pressure had reached the desired value.

III.2.3. Reactions in Monolayers and their Analyses

III.2.3.1. Reaction Conditions

There are two methods for depositing a film which will subsequently be reduced. It can either be deposited over a subphase that already contains the reducing agent, or it can be spread over a neutral subphase, which will then be infused with the reducing agent. When the latter method is used, portions of the film will be in contact with the reducing agent, while others (located in areas where the reducing agent has not yet diffused) will still be in contact with the neutral subphase. Such an inhomogeneity may produce questionable results. Therefore, this
method was only used when the reducing agent had to diffuse into a small volume of the subphase, such as when a film has already been compressed to a small molecular area. In this type of situation the diffusion of the reducing agent is expected to occur rapidly and should not introduce significant variations in product composition. We chose the first method for reduction of expanded films, and used both methods for reduction of compressed films.

III.23.2. Procedure for Film Recovery

After allowing the film to remain in contact with the reducing subphase for the allotted period of time, it was compressed rapidly and recovered using the aspirator trap. A dilute acid solution (15 mL of 0.05 M HCl) was placed in the aspirator trap prior to film recovery. This served to neutralize any of the basic subphase that was aspirated into the trap along with the film, thus destroying any NaBH₄ present and stopping the reduction. The teflon tubing and the aspirator trap were then flushed repeatedly with 10 mL portions of CH₂Cl₂. Each CH₂Cl₂ portion was used to extract the aqueous layer that was recovered from the aspirator trap in a separatory funnel. The combined CH₂Cl₂ extracts were evaporated with gentle heating under a N₂ stream. No attempt was made to dry the CH₂Cl₂ extracts using a drying agent because control experiments indicated that this caused a dramatic loss of the propellane diol products.
III.2.3.3. HPLC Analysis of the Recovered Film

A small amount of the starting material and the two product diols was added to the recovered sample of radioactive propellane. It was filtered for particulates (using a nylon 66 syringe tip filter, Rainin Instrument Co., Inc., Woburn MA) and it was dissolved in a small amount of the mobile phase prior to HPLC analysis. The mobile phase consisted of 65% hexane, 30% EtOAc, 5% IPr. The analytical (Si) Rainin Dynamax column was used at a flow rate of 1.5 mL/min. These conditions afforded the following retention times: anti ketol 4 min.; a,a diol 6.2 min.; s,a diol 12 min. The eluent corresponding to individual peaks was collected directly into polyethylene scintillation vials. Some of the eluent corresponding to the baseline after the last peak had eluted (14 min. after injection) was also collected. Scintillation fluid (Fisher Scientific; Scintiverse type II) was added to the vials (approximately 4 mL) and the activity was determined using a scintillation counter (Beckman model LS-5801). A set of standards were counted before counting the samples obtained from each analysis. The counter automatically counted for 10 min. or until the standard deviation of the activity reading was reduced to 2.

III.2.3.4. Methanol Reduction of [22.3.3]Propellane anti ketol

'H-labelled [22.3.3]propellane anti ketol solution (40 µL) was added to 1.5 mL methanol in a 5 mL conical vial equipped with a
magnetic stirring bar. 50 μL of a 2 M NaOH and 2 M NaBH₄ aqueous solution were added dropwise and the solution was stirred for 100 min. 60 μL of a 2 M aqueous HCl solution were added dropwise to neutralize the solution. The methanol was evaporated under a gentle N₂ stream and the flask was alternately washed with 1.5 mL portions of distilled H₂O and CH₃Cl, which were placed in a separatory funnel. The combined CH₃Cl extracts were evaporated under a gentle N₂ stream and subjected to the HPLC analysis described in the previous section.

III.3. Results

III.3.1. Films of [22.3.3]Propellanes

The π/A isotherm curve of the [22.3.3]propellane dione has a liftoff area of 68 Å²/molecule, a co-area of 64 Å²/molecule and collapses at 25 dyn/cm (Figure III.3.1). It displays a gradual phase transition at around 12-13 dyn/cm. A creep test indicated that this film is fairly stable (Figure III.3.2).

The [22.3.3]propellane syn ketol and anti ketol π/A isotherm curves are very similar to each other (Figure III.3.1). Both display a liftoff area of approximately 63.5 Å²/molecule. The syn ketol occupies a co-area of 61 Å²/molecule and collapses at 33 dyn/cm, while the anti ketol occupies a co-area of 62 Å²/molecule and collapses at 34 dyn/cm. Their isotherm curves seem to indicate that the films are undergoing many phase transitions, not being as
Figure III.3.1. [22.3.3]Propellane dione, ketol and acyloin π/A isotherms.

Figure III.3.2. [22.3.3]Propellane dione creep test @ 2 dyn/cm.
Figure III.3.3. [22.3.3] Propellane syn ketol creep test @ 2 dyn/cm.

smooth as that of the dione.

The ketol creep tests over a normal subphase indicated the films were fairly stable (Figures III.3.3 and III.3.4). Creep tests over a basic subphase (pH=12) however, indicated the films were very stable, displaying hardly any film creep at all (Figures III.3.5 and III.3.6). A creep test of the anti ketol over a pH=8 subphase, at a constant pressure of 20.5 dyn/cm led to an area reduction of approximately 10%, while at 2 dyn/cm it was reduced by 2 % after one hour (Figure III.3.7).

All three [22.3.3] propellane diol films showed good creep behavior, losing less than 3% of their initial molecular area after
Figure III.3.4. [22.3.3]Propellane anti ketol creep test @ 2 dyn/cm.

Figure III.3.5. [22.3.3]Propellane syn ketol creep test over a pH 12 subphase @ 2 dyn/cm.
Figure III.3.6. [22.3.3] Propylene anti ketol creep test over a pH 12 subphase @ 2 dyn/cm.

1 h at a constant pressure of 2 dyn/cm. However, isomer dependent differences could now be seen in the isotherms. The s,a diol π/A isotherm curve displays a liftoff area of 59 A^2/molecule, it occupies a co-area of 57 A^2/molecule and collapses at 35 dyn/cm (Figure III.3.8). Its isotherm curve displays a subtle transition point at around 14 dyn/cm. The π/A isotherm curve for a,a diol displays a liftoff area of 56 A^2/molecule, a co-area of 54 A^2/molecule and a collapse pressure of 35 dyn/cm. The isotherm curve displays a subtle transition point at approximately 14 dyn/cm (Figure III.3.8). The π/A isotherm curve for s,s diol displays a liftoff area of 59 A^2/molecule, a co-area of 54 A^2/molecule and a
Figure III.3.7. [22.3.3] Propellane anti-ketol creep test over a pH 8 subphase @ 2 and 20 dyn/cm.

Figure III.3.8. [22.3.3] Propellane a,a, s,a and s,s diol π/A isotherms.
Table III.3.1. χ/A Isotherm and creep test data for [22.3.3]propellanes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Lift-off area (Å²/mol.)</th>
<th>Co-area (Å²/mol.)</th>
<th>Coll. press. (dyn/cm)</th>
<th>% of init. mol. area after 1 hr from creep test @ 2 dyn/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>dione</td>
<td>68.0</td>
<td>64</td>
<td>25</td>
<td>95.5</td>
</tr>
<tr>
<td>syn ketol</td>
<td>63.5</td>
<td>61</td>
<td>33</td>
<td>96.5</td>
</tr>
<tr>
<td>anti ketol</td>
<td>63.5</td>
<td>62</td>
<td>34</td>
<td>98.0</td>
</tr>
<tr>
<td>s,s diol</td>
<td>59.0</td>
<td>54</td>
<td>33</td>
<td>97.0</td>
</tr>
<tr>
<td>s,a diol</td>
<td>59.0</td>
<td>57</td>
<td>35</td>
<td>99.0</td>
</tr>
<tr>
<td>a,a diol</td>
<td>56.0</td>
<td>54</td>
<td>35</td>
<td>97.5</td>
</tr>
</tbody>
</table>

collapse pressure of 33 dyn/cm. The isotherm curve displays a very prominent phase transition at around 3 dyn/cm (Figure III.3.8) and several more subtle ones at higher pressures. The results from the isotherms and creep tests of all the [22.3.3]propellanes are summarized in Table III.3.1.

III.3.2 Films of Acyloin and [12.3.3]Propellane dione

In order to compare the [22.3.3]propellane χ/A isotherms to related materials, we decided to study films composed of 2-oxocycloctetrasanol (acyloin) (Figure III.3.9) and [12.3.3]propellane dione.
Figure III.3.9. 2-Oxocyclotetracosanol (acyloin).

Figure III.3.10. [12.3.3]Propellane dione π/A isotherm on aqueous subphase; [12.3.3]propellane dione and [22.3.3]propellane dione π/A isotherms over a saturated NaCl subphase.

The π/A isotherm curve for the acyloin displays a liftoff area.
of approximately 52 A'/molecule, a co-area of 51 A'/molecule and a collapse pressure of 30 dyn/cm (Figure III.3.1). A rather prominent phase transition is seen at 11 dyn/cm and another one at approximately 22 dyn/cm.

The Π/A isotherm curve of [12.3.3]propellane dione over a plain aqueous subphase displayed a liftoff area of approximately 41 A'/molecule, its slope exhibited a very shallow rise and no collapse point was obvious (Figure III.3.10). The film formed was evidently not stable during the time scale of the Π/A isotherm. The Π/A isotherm curve, when repeated over a saturated NaCl subphase, displayed a liftoff area of 91 A'/molecule, a co-area of about 73 A'/molecule and a collapse pressure of 30 dyn/cm (Figure III.3.10). The isotherm curve displayed a phase transition at 11 dyn/cm.

The Π/A isotherm curve of [22.3.3]propellane dione over a similar saturated NaCl subphase displayed a liftoff area of 91 A'/molecule, a co-area of 73 A'/molecule and a collapse pressure of 33 dyn/cm (Figure III.3.10). The isotherm curve indicated phase transitions were occurring at 8 and 14 dyn/cm.

III.3.3 [22.3.3]Propellane-26-keto-29-anti-ol Film Reduction

The dione contains two ketone functionalities, each able to give rise to either the syn or anti alcohol upon reduction (Figure III.1.1). We decided to utilize anti ketol as the starting
Table III.3.2. Results of NaBH₄ reduction of [22.3.3]propellane anti ketol films.

<table>
<thead>
<tr>
<th>A² per molecule/dynes per cm</th>
<th>Relative amount NaBH₄</th>
<th>Rxn. time (hr)</th>
<th>% activity recovered</th>
<th>extent of reduction (% product)</th>
<th>% norm.**</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,350/0</td>
<td>2</td>
<td>2.0</td>
<td>48</td>
<td>93</td>
<td>81</td>
</tr>
<tr>
<td>180/0</td>
<td>1</td>
<td>5.0</td>
<td>47</td>
<td>98</td>
<td>78</td>
</tr>
<tr>
<td>180/0</td>
<td>1</td>
<td>13.5</td>
<td>8</td>
<td>93</td>
<td>82</td>
</tr>
<tr>
<td>180/0</td>
<td>1</td>
<td>1.5</td>
<td>23</td>
<td>74</td>
<td>76</td>
</tr>
<tr>
<td>60/2</td>
<td>1</td>
<td>5.0</td>
<td>30</td>
<td>97</td>
<td>76</td>
</tr>
<tr>
<td>60/2</td>
<td>2</td>
<td>1.5</td>
<td>38</td>
<td>97</td>
<td>75</td>
</tr>
<tr>
<td>* 60/2</td>
<td>2</td>
<td>2.0</td>
<td>19</td>
<td>69</td>
<td>78</td>
</tr>
<tr>
<td>* 55/20</td>
<td>2</td>
<td>2.0</td>
<td>74</td>
<td>69</td>
<td>75</td>
</tr>
<tr>
<td>** -</td>
<td>-</td>
<td>1.75</td>
<td>5</td>
<td>94</td>
<td>72</td>
</tr>
</tbody>
</table>

* base + NaBH₄ added after the film was under constant pressure
** methanol (bulk) reduction
*** a,a diol + s,a diol = 100 %

material, so that by having only one reducible ketone functionality per molecule it would be easier to analyze the ratio of diol products formed. Analytical, normal phase HPLC, gave baseline separation of the anti ketol (4 min) starting material from the a,a diol (6.2 min) and s,a diol (12 min) products.

The ³H-labelled anti ketol was used for monolayer reductions as well as for the bulk reduction. The amount of radioactivity
recovered varied from one experiment to another. We report (Table III.3.2) the extent of the reduction and the percent \( \text{a, a diol of the total amount of diol products recovered (normalized ratio).} \)

III.4 Discussion

III.4.1 [12.3.3] and [22.3.3]Propellane Films

Initial experiments involved the [22.3.3]propellanes. We reasoned that they had the greatest chance of generating stable monolayers due to the large polymethylene ring. We tested the [12.3.3]propellanes and found that they did not form stable Langmuir films on pure water subphases. During the isotherm a pressure increase was observed, but the isotherm curve exhibited a very shallow slope and a collapse point was never observed. An explanation for this behavior may be that the [12.3.3]propellane displayed enough hydrophobicity to initially form an expanded monolayer. However, as soon as the limiting area was approached and molecules came in contact with their neighbors (the start of the rise of the \( \pi/A \) curve), the resulting surface pressure destabilized the film and the molecules started dissolving into the subphase. This result is not totally unexpected, if we take into account Natrajian's observation that the [10.3.3]propellanes are sparingly soluble in water.\(^8\) Even if the monolayer forming material displays a slight solubility, the minute quantity of
material present in a monolayer and the large volume of water in the trough will cause most of it to dissolve.

In order to test whether the [12.3.3]propellane could be induced to form stable films, we decided to limit its solubility in the subphase by saturating the subphase with NaCl before spreading the [12.3.3]propellane monolayers. This technique has been used in other cases of slightly soluble film-forming materials. Following this treatment, [12.3.3]propellane dione displayed a more familiar-looking isotherm. When the isotherm of [22.3.3]propellane dione was measured under the same conditions, it was not the same as the one obtained over a pure water subphase, but it was very similar to that of [12.3.3]propellane dione over a saturated NaCl subphase.

The changes that are observed in the isotherm are probably due to the residual surface-active impurities introduced from saturating the subphase with so much NaCl. When the co-areas for the two isotherms were extrapolated, it was seen that they were essentially the same for both the [12.3.3] and [22.3.3]propellane diones. The fact that the limiting area for the two molecules is the same lends credence to the suggestion that the hydrophilic end of the molecule is composed of the bicyclooctane and its oxygen containing functionalities. This part of the molecule is the same for both the [12.3.3], and the [22.3.3]propellane diones. Studies involving the [12.3.3]propellane series would introduce the complications and inconvenience arising from having to use a NaCl-saturated water
subphase. Thus, we decided to focus our attention on the [22.3.3]propellane series, which formed stable monolayers over pure water.

III.4.2 2-Oxocyclooctacosanol (Acyloin) Films

Further evidence for the previously introduced hypothesis concerning the orientation of the propellane molecules at the air/water interface is provided from the π/A isotherms of the acyloin. This molecule is the [22.3.3]propellane precursor and has the same polymethylene ring that is present in a [22.3.3]propellane. However, it is missing the bicyclooctane portion. In the acyloin, the two carbon atoms that would form the bridgehead atoms in a propellane now have attached a carbonyl group on one and a hydroxyl group on the other and they form the polar base of the molecule.

The co-area extrapolated from acyloin isotherms is 20% smaller than that observed for propellane dione (Figure III.3.1). This reduction in the limiting area of the acyloin over that of propellane dione molecules is consistent with a picture of the propellanes oriented at the interface as described above. The hydrophilic portion of the propellane molecule is the bicyclooctane base and its carbonyl and/or hydroxyl groups, the hydrophilic portion of the acyloin is the hydroxyketone. The large
polymethylene ring acts as the hydrophobic group and is oriented away from the subphase surface for both types of molecules.

The observations from the study of cyclopentadecanone Langmuir films reported by Cadenhead and Demchak\textsuperscript{n} are in good agreement with our observations for acyloan films. They report that the $\pi/A$ isotherms of cyclopentadecanone films display a co-area of 45 A$^2$/molecule and collapse at approximately 15 dyn/cm. The increase to the 51 A$^2$/molecule co-area that we observed in the acyloan isotherm can be attributed to the larger polar head group of the acyloan (it contains a hydroxyl group $\alpha$- to the carbonyl that is not present in the cyclopentadecanone molecule). The larger size of the hydrophobic ring and the increased hydrophilicity of the head group combine to stabilize the acyloan monolayers. Thus, the slope of the $\pi/A$ isotherm curve is steeper for the acyloan (indicating a less compressible, or less water soluble film), and the collapse pressure increases to 30 dyn/cm.

III.4.3 [22.3.3]Propellane Film Characteristics

The $\pi/A$ isotherm data for the [22.3.3]propellanes point to an interesting feature. The dione has the largest co-area, followed by the ketols and finally the diols. The co-area is an indication of the space occupied by the amphiphile's head-group, and the head-group is similar among these molecules. This suggests that the conformation of the atoms present in the head-group is being
altered as we progress from dione, to ketols and finally to diols. It has been determined from our earlier structural work that the extent of the five-membered-ring pucker in the larger propellanes is a function of whether the ring itself is a ketone or alcohol, and whether it is fused to a ring bearing a ketone or an alcohol. Both cyclopentyl rings are flat for dione, ketols allow for slight pucker, and diols readily pucker the rings by as much as 40°.

Presumably, the area occupied by the flat cyclopentyl rings of the dione is somewhat larger than the minimum area which the polymethylene ring can occupy (>50 A²/molecule based on the acyloln). The cyclopentyl rings will not pucker however, and the film collapses at a lower pressure than the other propellanes. The ketols, and even more readily the diols, on the other hand, do pucker their cyclopentyl rings and better match the minimum area that the polymethylene ring occupies. This puckering and the molecular size adjustment it will cause could be responsible for the subtle phase transitions seen in the isotherms of these molecules, which are absent from the dione isotherm. Looking at the tabulated results of the isotherms (Table III.2), we notice that dione has the largest co-area (64 A²) and the lowest collapse pressure (25 dyn/cm). The ketols pucker enough to allow the co-area to shrink to 61-62 A², and the collapse pressure now rises to 33-34 dyn/cm due to the formation of a better packed film. The diols with their even more facile puckering produce even smaller
co-areas, while keeping a collapse pressure of 34 dyn/cm. It seems that the minimum area that the polymethylene ring will occupy is 56-60 Å². Thus, our attempts to form films from the acyloin suffered both from its lack of rotational constraints within the film, as well as from its lack of a suitable "base" to sit on the water surface and fill the necessary 56-60 Å². Therefore, its films show a somewhat lower collapse pressure and many secondary phase transitions.

The x/A isotherms also indicate that some interesting behavior could be taking place among the diols. The co-area of the s,s diol is the same as that for the a,a diol (54 Å²), but both are smaller than the s,a diol co-area (57 Å²) (Figure III.3.2). Among the diols, the a,a diol is the only one capable of intramolecular hydrogen bonding by bending both cyclopentyl rings away from the polymethylene ring; this type of behavior would lead to a decreased molecular area in a monolayer of the material. The intramolecular hydrogen bond in the a,a diol could be forming while the molecule is still dissolved in CHCl₃. The extent of flexibility present in the cyclopentyl rings of the diols is indicated by the fact that the s,s diol can pucker its cyclopentyl rings (to form intermolecular hydrogen bonds with neighboring molecules perhaps) enough to attain the same molecular area seen with a,a diol. The s,a diol however cannot pucker its cyclopentyl rings enough and ends up with a slightly larger co-area. Also of interest is the
reproducible "step" seen low (<5 dyn/cm) in the s,s diol π/A isotherm, which is attributed to a phase transition. The liftoff area of its π/A isotherm is similar to that seen for the s,a diol isotherm. This however, is soon followed by the "plateau" of the phase transition, after which the isotherm curve of the s,s diol is very similar to that of the s,a diol. This could indicate that the packing attained by the s,a diol is initially energetically favorable for the s,s diol too, but, as soon as the surface pressure rises a little, it can undergo a phase transition that lets it attain a different packing arrangement.

Beyond examining the shape of the various isotherms, we noted that the stability of the [22.3.3]propellane anti ketol films was altered when the subphase pH was changed, as shown by changes in their creep test behavior. This observation could lead to an understanding of the film destabilization mechanism during the creep test. The NaOH that is added to the subphase to raise its pH could lead to increased interactions between the ketone of the anti ketol and the water molecules in it. This will likely increase the hydrophilicity of the polar group, thus stabilizing the film. If the [22.3.3]propellane anti ketol was even in the least bit water soluble, this increased interaction between the polar head group and the subphase would lead to increased solubility, thus destabilizing the film. This is not occurring. The likely mechanism for film destabilization (leading to the observed creep
behavior) in the absence of the added NaOH, may thus be a "squeezing-out" of molecules from the compressed film, due to the low hydrophilicity of the polar head group.

The fact that [22.3.3]propellanes form stable films at the air/water interface indicates that they achieve efficient filling of space in the plane of the monolayer. In order to gain a better understanding of the shape of these molecules, X-ray crystallography data were used to construct a model of the [12.3.3]propellane dione. This model was then used to examine the packing of our propellane head groups at the air/water interface.

By using a combination of the CHEMGRAF (created by E. K. Davies; distributed by Chemical Design Ltd, Oxford) and CHEMLAB (developed by A. Hopfinger) computer packages on a VAX 785, the propellane model could be rotated, so that it could be viewed from all directions and space filling depictions could be generated. Atomic radii 20% larger than the default radii provided by CHEMLAB were used in the construction of the space filling models, to allow for added space between molecules and small motions of the various atoms. The radii used were the following (in Å) C(sp') 1.98, C(sp') 1.80, O(sp') 1.62, H 1.5.

By combining perpendicular views that were rotated by 90° relative to each other, the one dimensional packing model depicted in Figure III.4.1 was generated. In this one dimensional model efficient filling of space is obtained by rotating each molecule by
Figure III.4.1. One dimensional packing model for propellane diones.

90° relative to its two nearest neighbors. A variety of approaches can be followed in extending this model to encompass the two dimensional filling of space in the monolayer. One of the simplest, in light of the very similar dimensions for the width of the molecule in both of its side views (9.4 and 9.7 A) (Figure III.4.1), is to allow a square 8 A long for each of the propellane molecules. Thus, the space occupied by each molecule is $64 \text{ A}^2$, the same as the co-area of the [22.3.3]propellane dione, and the one dimensional packing model depicted in Figure III.4.1 is extended in both the X and Y directions. Figure III.4.2 depicts the view from above the film for the "square packed" array that is obtained in this manner and Figure III.4.3 depicts the array the way it would look from beneath the interface. Alternatively, a row of propellane molecules can slip, to allow for better filling of space. Figure III.4.4 depicts the view from above the film of a "slip packed" array and Figure III.4.5 depicts the view from below
Figure III.4.2. Top view of the "square packed" array of propellane molecules at the air/water interface.

Figure III.4.3. Bottom view of the "square packed" array of propellane molecules at the air/water interface.
Figure III.4.4. Top view of the "slip packed" array of propellane molecules at the air/water interface.

Figure III.4.5. Bottom view of the "slip packed" array of propellane molecules at the air/water interface.
the interface.

III.4.4 HPLC Analysis of Recovered NaBH₄-Reduced Films of [22.3.3]Propellane-26-keto-29-anti-ol

Radioactive labelling coupled with an HPLC separation provided us with a very sensitive technique by which we could analyze the results of the reduction. Extra amounts of non-³H-labelled anti ketol, a,a diol and s,a diol were added to the recovered film prior to HPLC analysis, so that there would be enough material present for RI detection. However, the activity present in any HPLC fraction would only be due to the reduction (or lack thereof) of the ³H labelled material in the Langmuir film. The ratio of diol products obtained from the reduction of [22.3.3]propellane anti ketol might vary depending on the reduction environment and the extent of molecular organization present. We were very interested in determining what the effect of constraining the propellanes at the air/water interface would be on the ratio of diol products formed. Langmuir films represent a system where the molecules are more ordered than in any other system in which this reduction has been studied, and we expected this to affect the product ratio.

We found that in all experiments where the propellane film is expanded, the percent a,a diol formed is equal to 79 ± 3%. When the film is compressed to a measurable surface pressure and the propellane molecules are in close proximity to one another however,
the percent a,a diol formed is equal to 76 ± 2%. The bulk reduction in methanol, which is a good approximation of the product distribution in the absence of a specific molecular organization or orientation, led to the formation of 72% a,a diol. The margins of error are such, that we cannot say with certainty whether a difference exists between the ratios of diols formed under expanded and compressed film conditions without performing many duplicate experiments. The percent diol formed from propellane reduction in a monolayer is closer to that observed for the bulk reduction than for the reduction in the presence of a micelle. We can state that from the point of view of the B₄H₄ molecule, the accessibility of the ketone functionality of a propellane constrained at the air/water interface is similar to that of a propellane dissolved in methanol. This would indicate that the hydrophilic part of the propellane is not simply in contact with the interface, but is actually submerged to a fair extent, allowing the B₄H₄ access to both sides of the bicyclooctane base.

III.5 Conclusion

We have shown that [22.3.3]propellanes form stable, well ordered films at the air/water interface. A model has been proposed which might lead to an understanding of how these unusually shaped molecules orient themselves at the interface and how they efficiently fill space in a monolayer. The borohydride
reduction of [22.3.3]propellane ketol monolayers has been performed and the product ratio obtained compared to the same reduction both in the presence and absence of other types of organized media.
References

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