♣Thermal Oxidation of Lipids in Monolayers.
I. The Nature of Binding on Silica

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ABSTRACT

The purpose of this study was to investigate whether the oxidation of lipids in the ordered state differs from that in the bulk phase. Simple model systems of lipids adsorbed on silica were used as a monolayer model system. This part of the study was designed to provide a better understanding of the nature of lipid adsorption on silica. Isotherms were determined for a number of substrates differing in chain length and functional groups. The number of molecules adsorbed per unit area of silica was found to decrease with increasing chain length. Binding was also dependent on the type of functional group present. For the same length, the amount adsorbed was in the following order: alcohol > acid > ester, whereas binding strength was as follows: acid > ester > alcohol.

INTRODUCTION

Bulk phase oxidation of lipids has been studied extensively. However, in biological systems such as cell membranes, the lipid molecules are highly ordered. The question arises whether mechanisms of oxidation in bulk, and the resulting reaction products, differ from those in the ordered state.

Because the study of ordered lipid molecules as they exist in their native state is extremely complex, many investigators used simpler model systems to provide information which may be applicable to the more natural systems. In our laboratory, a study was initiated in which different fatty acid esters adsorbed on silica were used as a model system of monolayers. In this report, the nature of adsorption of substrates varying in structure, chain length, functional groups and unsaturation is described.

MATERIALS AND METHODS

Materials

The substrates, octanol, octadecanol, octanoic acid, octadecanoic acid, oleic acid, linoleic acid, ethyl octanoate, ethyl stearate and ethyl linoleate, were purchased in the highest available purity from Sigma Chemical Company, St. Louis, Missouri. These were used without further purification. Silica gel G was purchased from Applied Science Laboratories Inc., State College, Pennsylvania. The material had a particle size of 10-40 μ and contained about 13% calcium sulfate as binder. The specific surface area of the silica gel was 335 m/g as determined by the BET method by Pacific Sorption Service, Chico, California.

Determination of Adsorption Isotherms

Lipid monolayers were prepared according to the procedures described by Porter et al. (1) and Wu and Mead (2), with minor modifications. Various concentrations of each substrate in 100 ml of pentane were each added to 6 g silica and stirred for one hr to achieve equilibrium. Substrate concentration in the supernatants was determined gravimetrically after solvent evaporation. From the initial and final concentration, the amount of substrate adsorbed per gram of silica was determined. In some cases, where the substrates were too volatile to provide accurate gravimetric analysis, e.g. octanol and ethyl octanoate, gas chromatography (GC)

was used. Gc and gravimetric methods gave similar results as confirmed with ethyl stearate and ethyl linoleate (Table I). Conventional saturation curve, Langmuir and Scatchard plots for each substrate were used to determine the binding constants and maximum amounts of binding for each substrate.

RESULTS AND DISCUSSION

For all the substrates used, the binding curve showed that the amounts of substrates bound are saturable on the silica surface. Both Langmuir and Scatchard plots gave straight lines, suggesting there is a limiting number of binding sites on the silica surface for each substrate (Fig. 1). The binding constant (slope) and maximum number of binding sites (x-axis intercept) are obtained from the Scatchard plot.

The binding constants were based on the line which best fits all the concentration data. The correlation coefficients for all lines were greater than 0.95. For some substrates, the plots show inflection points (Table II).

It can be seen that for all substrates, the number of moles adsorbed per unit area of silica decreases as the chain length increases. Among different classes of compound with the same chain length, the amount of substrate adsorbed decreases in the following order: alcohol > fatty acid > ethyl ester. Among the classes of substrates of the same chain length, the binding constant (K_{eq}), which is an indication of the binding strength, decreases in the following order: fatty acid > ethyl ester > alcohol.

The fact that all the substrates used in this study show saturable binding to silica with limited binding sites for each substrate suggests a monolayer binding to the silica surface. The monolayer nature of the binding on silica also has been suggested by Porter et al. (1) and Wu and Mead (2).

Wu and Mead (2) used C16, C18:1 and C18:2 acids and their derivatives and found that the number of molecules adsorbed corresponds to the number of isolated non-hydrogen-bonded silanol groups. They also concluded that binding is insensitive to unsaturation and chain length of the substrates. In contrast, the present study shows that both the binding constants and the maximum bonding are influenced by the type of functional groups present (Table II). In addition, the data obtained indicate that the tendency to form hydrogen bonds corresponds to the order of adsorption, i.e., the higher the tendency for hydrogen bonding, the stronger the adsorption.

TABLE I

Comparison of GC and Gravimetric Methods for the Determination of Substrate Binding to Silica Gel G

Substrate	Gas chromatographic (mmol/g silica)		Gravimetric (mmol/g silica)	
	Mean[a]	s.d.[b]	Mean[a]	s.d.[b]
Ethyl stearate	0.59	0.02	0.57	0.03
Ethyl linoleate	0.43	0.02	0.42	0.02

[a]Two determinations.
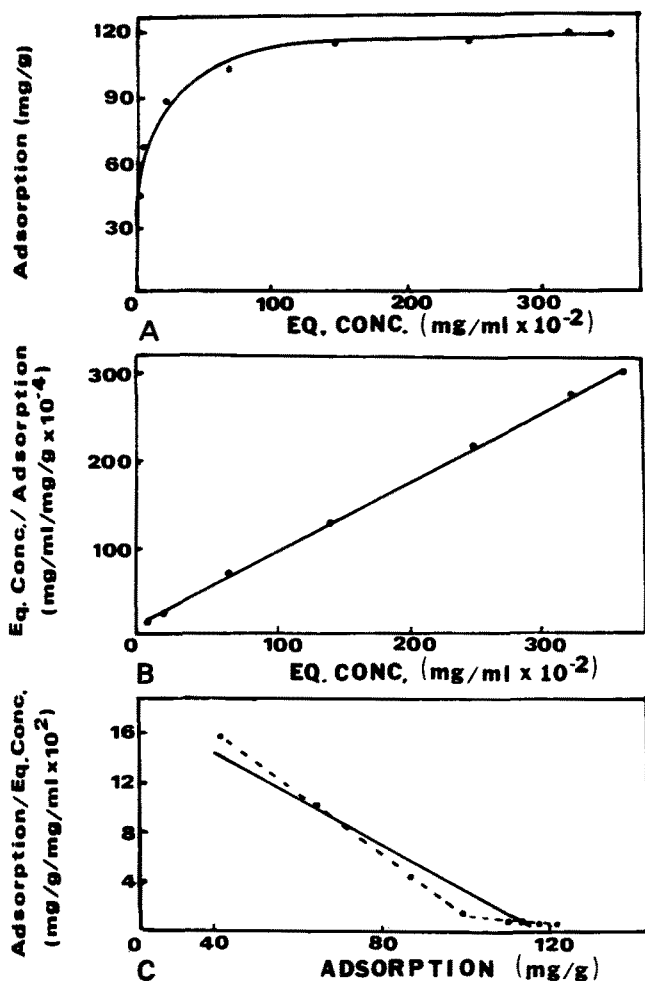[b]Standard deviation from the mean.

FIG. 1. Binding of octanoic acid to silica gel G. A, conventional adsorption isotherm; B, Langmuir plot, and C, Scatchard plot.

TABLE II

Binding Constants and Maximum Binding Amounts for Different Substrates on Silica Gel G

|	Binding constant (k_{eq})	Maximum binding (mmol/g silica)	
		Mean	s.d.
Alcohols			
Octanol	1.1	1.35	0.03
Octadecanol	2.1 (3.6, 1.7)[a]	0.95	0.02
Acids			
Octanoid acid	21.3 (10.5, 72.5)[a]	1.23	0.03
Stearic acid	7.0	0.75	0.04
Oleic acid	5.8	0.73	0.02
Linoleic acid	7.7	0.76	0.01
Esters			
Ethyl octanoate	4.0	0.67	0.01
Ethyl stearate	2.7	0.57	0.01
Ethyl linoleate	3.4	0.42	0.02

[a]Reflection point.

Several investigators have shown that hydrogen bond formation between electron negative atoms of π electrons of the substrates and the silanol groups on the silica surface play a major role in adsorption (3).

Marshall and Rochester (4) used IR to show that the interaction between acid monomer and surface silanol groups probably is best represented as follows:
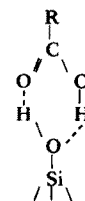
On the other hand, alcohol might form the hydrogen bond with silanol groups on the silica surface as:

or
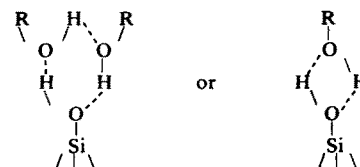
One acid molecule can form two H-bonds with a silanol group. Although an alcohol also can form two H-bonds with a silanol group, at higher concentrations of alcohol two alcohol molecules might compete for the same silanol group. It would be more difficult for two carboxyl groups to bind to one silanol group because of their bulkiness. This may explain why acid binds more strongly than alcohol. On the other hand, every silanol group can bind two molecules of alcohol but only one molecule of fatty acid. This might be the reason alcohols bind more than fatty acids.

Molecular size and shape are important factors in adsorption because stearic hindrance can prevent hydrogen bonding and hence adsorption on the silica surface (3).

Because of the bulkiness of the ester group, hydrogen bonding between esters and silanol groups would be weaker than that for acids. As with acid, it seems unlikely to have two ester molecules bind to the same silanol group via hydrogen bonding.

Hoffman et al. (3) found that for C1-C4 alcohols, the surface areas covered by the adsorbed molecules on silica were in the following order: methanol > ethanol > 1-propanol > 1-butanol.

Bonetzkaya and Krasilnikov (5) also found that adsorption of an homologous series of alcohols from nonpolar solvents on silica gel has the same tendency. Bartell and Scheffler (6), Kiselev and Vorm (7) and Elder and Springer (8) also reached similar conclusions for fatty acids. It is obvious that the area occupied by a molecule in the surface layer depends on the chain length. The fact that the number of molecules adsorbed per unit area of silica decreased as the chain length increased (Table II) may be explained by the possibility that rotation of the long chain fatty acid might cover larger surface areas, thus preventing the molecules from packing closely together.

As indicated above, the surface area for the silica gel G used in this study was 335 m^2/g. The maximum adsorption for linoleic acid is 190 mg/g silica. At maximum adsorption, Porter et al. give 260 mg of linoleic acid per g silica for an area of 450 m^2/g, while Wu and Mead (2) give 220 mg/g for an area of 378 m^2/g. The area/molecule value reported here is very close to both Porter's and Wu and Mead's values, i.e. 80 $Å^2$/molecule. Langmuir (9) reported a cross sectional area of 22 $Å^2$ for stearic acid with the molecular chain perpendicular to the water surface and the polar carboxyl group oriented toward the water surface. Moreover, linoleic acid lying flat would require 143 $Å^2$/molecule (10) which is

much larger than the area obtained at the maximum adsorption on silica. This appears to indicate that linoleic acid monolayers are neither a closely packed array of fatty acid molecules, as in the case of the air-water interface, nor lying flat on the silica surface (2).

It should be pointed out, however, that for most adsorbents the values obtained for surface area are dependent on the cross-sectional area of the molecules used for monolayer coverage. This is due to the fact that small yardsticks, e.g. nitrogen, can follow many more of the fine details of an irregular surface than larger molecules, e.g. stearic acid, and consequently give relatively large surface area values (12, 13). Avnir and Pfeifer (14) reported a fractal dimension of 2.94 for silicic acid, reflecting the labyrinthine nature of this adsorbent, and concluded that molecules adsorbed on silicic acid may thus experience a nearest-neighbor geometry that resembles that of a three dimensional, rather than a planar array of the adsorbate. It can be seen that the surface available for monolayer binding of stearic or linoleic acid molecules on silica may be far less than indicated from measurements made with nitrogen as a probe molecule (BET).

The reflection points observed in the Scatchard plots of some substrates suggest that two different binding constants may be involved for one substrate. From IR studies, it has been shown that, at low surface coverage, adsorption of acid monomer onto pairs of adjacent silanol groups occurs. As the concentration of acid in solution increases, adsorption of monomer onto isolated surface silanol groups becomes predominant. Therefore, it is possible that there are two different forms of binding between substrate and silica. Either the same substrate binds at different sites, e.g. paired silanol groups and isolated silanol groups, or different forms of substrate bind to the same site with different

binding strengths, e.g. monomer at low concentration and dimer at high concentration as described previously for alcohol.

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♣Sunflower Oil Diesel Fuel: Engine Wear Implications

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ABSTRACT

Diesel lubricating oil contaminated with sunflower oil fuel was degraded under conditions simulating an engine crankcase environment for metal wear testing. Wear analyses were performed using a four-ball apparatus according to ASTM D 4172. Lubricity of oils was characterized by ball scar dimensions. Contaminated lubricating oils exhibited lower metal wear indexes than pure lube oil control samples, even when the former were severely degraded as measured by thickening and loss of alkaline reserve.

INTRODUCTION

Seed oils such as sunflower ultimately may prove acceptable as substitute diesel fuels in emergency situations. However, a variety of problems including unburned fuel contamination of engine lubricating oil must be solved first. Unsaturated seed oils undergo addition polymerization and acid-forming oxidation reactions at conditions present in a diesel crankcase environment (1), leading to thickening and a loss of alkaline reserve in lubrication oil.

In an earlier paper (2), we reported the polymerization thickening and loss of alkalinity of SAE 30 diesel lubricating oil contaminated with 5.0% sunflower oil when the mixture was exposed to simulated engine conditions; cf. (2) for a

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complete description of experimental apparatus and procedures. Sample mixtures were treated for up to 70 hr at 150 C in an immersion bath heater. Oxygen was percolated vigorously through test cells of contaminated oil in the presence of metallic copper catalyst. Viscosity rise and alkalinity loss responses are shown in Figure 1. Viscosities given were determined at 40 C; alkalinity as expressed is a total base number (TBN) according to ASTM D 2896 (3).

The thickening and alkalinity losses shown in Figure 1 pose definite lubricant distribution and possible corrosion problems for a diesel engine in extended operation on sunflower oil fuel. After only 30 hr exposure to a simulated crankcase environment, viscosity is increasing sharply and alkaline reserve is largely exhausted. An additional problem of progressive decline in lubricity for degraded oil mixtures has also been widely speculated, but reliable in-engine testing of the wear preventive characteristics of contaminated lubrication oil is costly and difficult (4).

RESULTS AND DISCUSSION

Oil mixtures degraded as shown in Figure 1 were tested for lubricity according to ASTM D 4172, "Wear Preventative Characteristics of Lubricating Fluid (Four-Ball Method)."