

Reactivity of Carboxy Esters in Gold–Thiol Monolayers

Partha Neogi, Sujata Neogi and Charles J. M. Stirling*

Department of Chemistry, The University of Sheffield, Sheffield, UK S3 7HF

The reactivity of gold–thiol monolayers with carboxy ester functions at controlled distances from the surface is sensitive to this distance when this is highly ordered; such surfaces are inert to pig liver esterase, which accumulates, however, on both hydrophilic and hydrophobic surfaces.

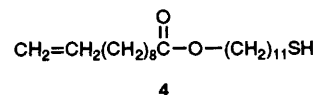
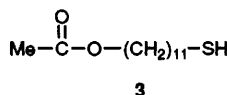
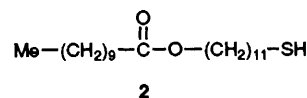
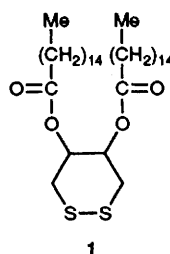
Long chain alkanethiols are chemisorbed spontaneously from solution on to gold surfaces to form ordered monolayers, by self assembly.¹ Most previous studies on self-assembled monolayers have focused on their physical structure and surface properties and only a few reports on chemical properties have appeared. Attempts to transesterify the film of disulfide **1** by Nuzzo and coworkers² were unsuccessful. Ulman and coworkers³ treated a chemisorbed monolayer of 11-hydroxyundecanethiol on gold with octadecyltrichlorosilane forming a second (hydrophobic) layer. Recently, conversion of alkanethiol monolayers on gold with a carboxy chloride function in the surface to (surface) amido and ester groups has been reported.^{4a,b}

We now report on the differences of reactivity between highly ordered and less ordered monolayers with carboxy ester functions in the surface. Such films were prepared by using gold mirrors deposited on different surfaces. Highly ordered films (type A) were prepared using surfaces obtained by plasma evaporation of gold (100 nm) onto polished silicon wafers primed with an adhesion layer of chromium (5 nm). Less ordered films (type B) were prepared on mirrors deposited by plasma evaporation of gold on to clean glass slides, also primed with chromium.^{†‡} Examination of the plasma gold–silicon surfaces by atomic force microscopy (AFM) showed surface roughness of *ca.* 10 Å. Immersion of the mirrors in solutions of esters **2** and **3** (10^{-3} mol dm⁻³ in EtOH) gave self-assembled monolayers. Polarised reflectance–absorbance FTIR spectra§ of such monolayers of **2** and

3 are shown in Fig. 1. Water contact angles¶ of 112° on type A and of 110° on the type B surface were observed for ester **2**. Ester **3** gives contact angles with water of 63° on silicon and 62° on glass.

Transesterification with methanolic sodium methoxide (0.1 mol dm⁻³) at 20 °C was monitored by the disappearance of the carbonyl absorption at 1740 cm⁻¹ and change of contact angle. The highly ordered film of long chain ester, **2**, on type A surfaces did not transesterify under these conditions Fig. 1(a). The intensity of the carbonyl peak in the IR spectrum and the water contact angle of the film showed no observable change even after three weeks. A film of the same ester on type B surfaces showed a half-life for transesterification of 4 days.

In contrast to the long chain ester, **2**, reaction with methanolic sodium methoxide (0.1 mol dm⁻³) of self-assembled layers of short chain ester, **3**, on both surfaces occurred readily Fig. 1(b). Reaction of the monolayer on surface A shows a half-life of 3 h compared with 2 h on type B surfaces, reactions again being monitored by loss of carbonyl group



† Plasma coating was carried out with a Microvac 350 coater (Ion Tech Ltd). The coater was evacuated to a vacuum of 10^{-6} mm and flushed with argon three times before coating. Thicknesses were monitored with a piezoelectric quartz crystal.

‡ Prior to evaporation, silicon wafers and glass slides were washed first with Decon and rinsed with distilled water. They were then placed in $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2$ (30 vol) (7:1) at 100 °C for 1 h. (CARE!) They were then rinsed with distilled water, dried in a stream of argon and coated immediately.

§ Polarised reflectance–absorbance FTIR spectra of monolayers were recorded on a Perkin-Elmer 1725X spectrophotometer fitted with a mercury-cadmium-telluride (MCT) detector cooled in liquid nitrogen.

¶ Sessile contact angle measurements with water were performed in a chamber saturated with water vapour. Flat end hypodermic needles were employed to place drops (1 μl) on the surface which was then observed with a cathetometer fitted with a graticule.

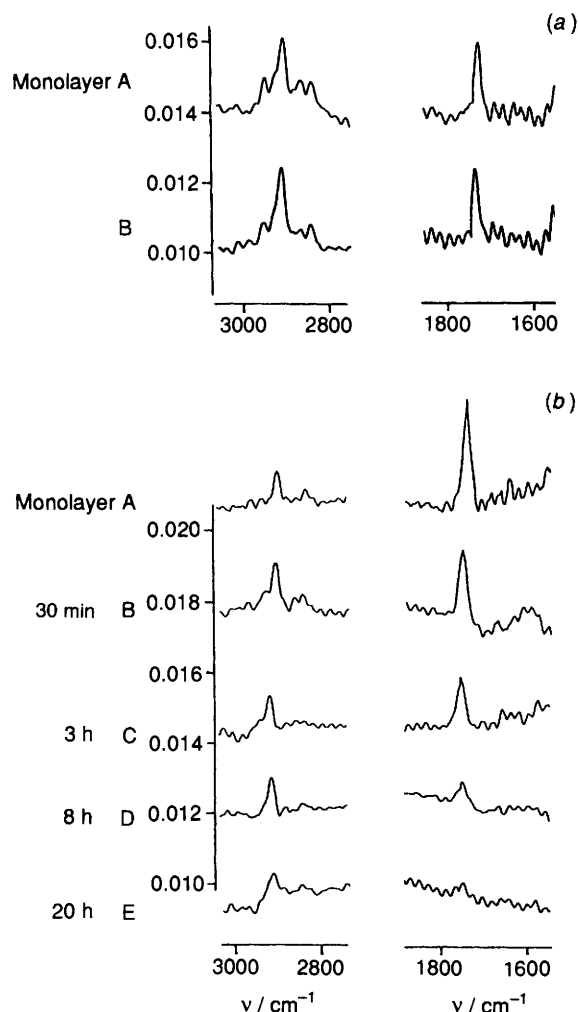


Fig. 1 Polarised reflectance absorbance FTIR spectra of (a) ester 2: A, monolayer; B, after exposure to 0.1 mol dm^{-3} NaOMe–MeOH for 21 days. (b) Ester 3: A, monolayer; B–E, after exposure to 0.1 mol dm^{-3} NaOMe–MeOH for the times indicated.

intensity and decrease of water contact angle. These observations suggest that penetration of surfaces by methoxide ion to a deeply buried functional group, in well-ordered monolayers, is not possible, whereas for loosely packed films on type B surfaces, methoxide ion can penetrate to attack the ester function. In bulk solution at 20°C , transesterification^{||} of ester 2 by methanolic sodium methoxide was 3.5 times slower than that of ester 3.

We have also examined the reactivity of these ester-functionalised surfaces with a hydrolytic enzyme. Films of esters 2 and 3 on type B surfaces were treated with buffered suspensions of pig liver esterase (PLE).^{5**} No reaction was observed either for the long chain ester 2 or for the short chain ester 3. In preliminary experiments with esters 3 and 4

^{||} Bulk solution transesterifications were carried out at $20 \pm 0.2^\circ\text{C}$. Aliquots ($20 \mu\text{l}$) of reaction mixtures were injected directly onto an HPLC column (Spherosorb ODS 9:1 acetonitrile water and RI detector).

** Pig liver esterase was used as supplied by Sigma and all reactions were carried out in 0.2 mol dm^{-3} phosphate buffer at pH 7 at 20°C . Coated mirrors were immersed in a suspension of PLE (0.1 ml) in buffer (100 ml) and were removed at intervals. They were washed thoroughly with ethanol and water and dried under vacuum before examination.

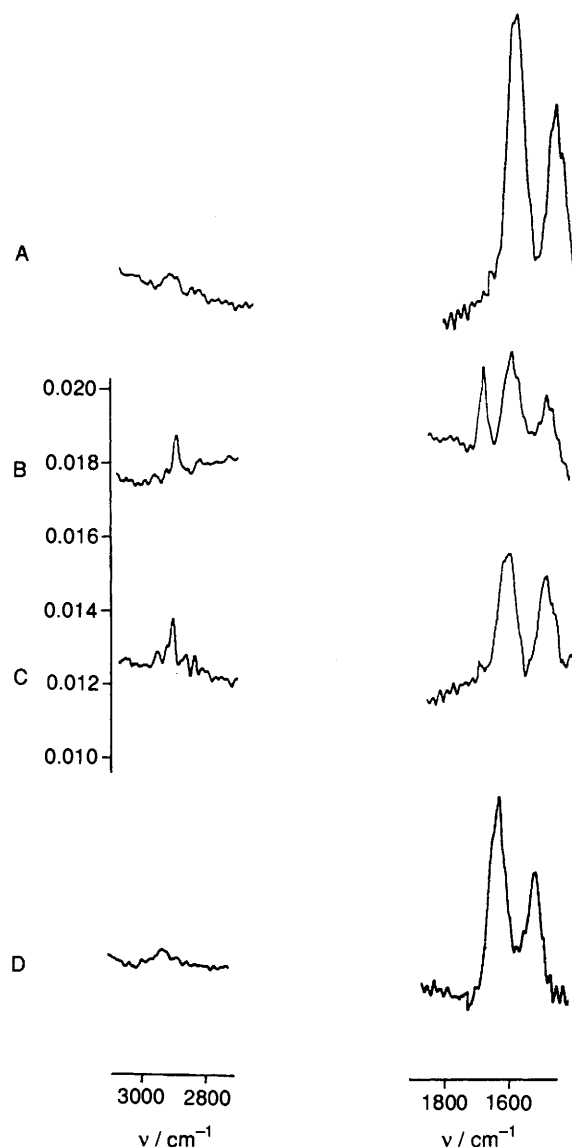


Fig. 2 Adhesion of PLE to surfaces: (A) clean gold film, (B) monolayer of ester 3, (C) monolayer of 11-hydroxyundecanethiol and (D) monolayer of octadecanethiol

deposited on gold surfaces sputtered onto glass, and probably much rougher than type B surfaces, both films were found to react with PLE, the latter reacting *ca.* 10 times more slowly than the former.

A further observation in relation to PLE hydrolysis is that the enzyme becomes very strongly attached to the film surface irrespective of whether these are of short (hydrophilic) or long chain (hydrophobic) esters.†† Strong amide I and II bands⁶ at 1660 and 1548 cm^{-1} develop with time (Fig. 2). This tendency of PLE to bind with the surface was found to be independent of the nature of monolayer film. Monolayers of octadecanethiol and of 11-hydroxyundecanethiol showed similar binding of enzyme to the surface.

We thank the University of Sheffield for support of this work, Dr S. Thorpe (HSE, Sheffield) for help with plasma

†† The referees comment that this is a common experience on the macroscale and is probably due to non-specific hydrophobic binding with precedent in, for example, interactions of lipases and esterases with hydrophobic column supports in lipase purification.

gold deposition and Mr David Andrews for advice on FTIR spectroscopy.

Received, 12th March 1993; Com. 3/01447I

References

- 1 C. D. Bain, E. B. Troughton, Yu-Tai Tao, J. Evall, G. M. Whitesides and R. G. Nuzzo, *J. Am. Chem. Soc.*, 1989, **111**, 321.
 - 2 R. G. Nuzzo, F. A. Fusco and D. L. Allara, *J. Am. Chem. Soc.*, 1987, **109**, 2358.
 - 3 A. Ulman and N. Tillman, *Langmuir*, 1989, **5**, 1418.
 - 4 (a) H. Keller, W. Schrepp and H. Fuchs, *Thin Solid Films*, 1992, **210**, 799; (b) R. V. Duevel and R. M. Corn, *Anal. Chem.*, 1992, **64**, 337.
 - 5 M. Eberle, M. Missbach and D. Seebach, *Org. Synth.*, 1990, **69**, 19.
 - 6 E. Pretsch, W. Simon, J. Seibl and T. Clerc, *Tables of Spectral Data for Structure Determination of Organic Compounds*, Springer, Berlin, 1989.
-