Reactions in Monolayers: The Oxidation of Thiol to Disulfide at Various Initial Surface Pressures

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Oxidation of 1-octadecanethiol monolayer on air-water interface by acidified potassium hexacyanoferrate(III) contained in the sub-phase is described. Since the surface pressure for the compressed monolayer of the thiol depends linearly on its surface concentration, the rate of this reaction can be studies by following the decrease in surface pressure with time. For intermediate values of the initial surface pressures, the pseudo-zero order rate constant varies within a relatively narrow range (< ± 7 %). In extremely compressed monolayers, the reaction is slower by up to 60 %. This has been interpreted in terms of a squeezing out of the sub-phase oxidant from the monolayer region as well as the unfavourable orientation of the reacting thiol group.

Key Words: Oxidation, Disulfide, Monolayers, Surface pressures, Thiol.

INTRODUCTION

Reactions between monolayers (spread on air-aqueous solution interface) and the sub-phase have provided a novel opportunity to examine and control the reactivity of molecules[1-14]. In such systems, surface pressure, π, can affect reactivity, since π determines how the molecules in the surface films are oriented in space. If, for example, the reacting functionality in the monolayer is remote from the hydrophilic head group, this functionality may be made inaccessible to the sub-phase by compressing the film to a higher surface pressure[1,2], making the monolayer less reactive with the underlying solution. By contrast, reactions occurring at a single center, *e.g.*, the chromic acid oxidation of 1-phenyl-1-hexadecanol[4] and the base-catalyzed hydrolysis of an octadecyl ester[5] are not significantly affected by surface pressure changes.

One of the reactions that have been studied in such a setting is the oxidation of 1-octadenethiol to dioctadecyl disulfide[10,11]. This system is of interest since thiols and disulfides are important compounds in many biological redox systems. For example, thiol group in cysteine has a unique role in protein structure owing to its facile oxidation to cystine leading to the cross-linking of protein chains. These studies compared the kinetics of oxidation in an expanded monolayer with that in a

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compressed film, with and without a catalyst. It was found that in an expanded monolayer the reaction is pseudo-first order, while in a compressed layer it was pseudo-zeroth order if the surface pressure was kept constant. The previous studies were confined to monolayers that were either fully expanded (with surface pressure near zero) or highly compressed, while the present study enlarges the scope to include films with various states of initial compression. In the present study, 1-octadecanethiol (**1**) was spread over an acidified solution of potassium hexacyanoferrate(III), $K_3Fe(CN)_6$ and the progress of oxidation to dioctadecyl disulfide (**2**) was followed by monitoring the decrease in surface pressure with time. The disulfide, not being surface-active, desorbs as it is formed and the reaction results in a decrease in surface pressure.
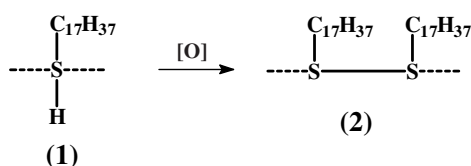
EXPERIMENTAL

All water used was obtained by taking de-ionized water and doubly distilling it using a two-stage quartz still. The sub-phase was prepared by dissolving the required mass of potassium hexacyanoferrate(III), Fluka (Puriss) in 0.001 molar HCl to get a solution of the required concentration. 1-octadecanethiol (98 %) was commercially available from Aldrich and used without further purification. The hexane used was HPLC grade, supplied by Fluka.

The reaction was carried out in a rectangular trough (manufactured by Nima Technology, Coventry, UK) made out of PTFE. This is essentially a modified Langmuir trough, with dimensions 30 cm × 20 cm × 0.5 cm, fixed onto an aluminum base through which water can be circulated from a thermostated bath. The apparatus has two independently movable PTFE barriers that can be used to vary the surface area, whose value is displayed digitally. Near one end of the trough was a Wilhelmy plate, made of a filter paper, connected to a sensor whose output signal could be calibrated in terms of the surface tension acting on the plate. The surface pressure was digitally displayed and read to 0.1 mNm^{-1}.

Kinetics: In a typical run, one of the barriers is positioned near one end and the other (compression) barrier is placed near the middle of the trough. The trough was filled with 1×10^{-4} M potassium hexacyanoferrate(III) solution in 0.001 M HCl at 25 ± 0.1 ºC and the surface was swept by moving the compression barrier over the entire surface and applying suction at the solution-air interface to remove any adsorbed impurities. The acid acts as a catalyst. The compression barrier is then positioned such that the area enclosed between the barriers is about 300 cm^2. A suitable quantity of a 2.40×10^{-3} M thiol solution in hexane was then added drop-wise

to the surface using a Hamilton microliter syringe. The solution was seen to spread and the solvent was allowed to evaporate. After *ca.* 6 min the film was compressed to the desired initial surface pressure for each run. The value of the surface pressure was displayed on the computer screen and a graph was generated between surface pressure and time. The surface pressure was measurable to an accuracy of ± 0.5 mN/m. The measurements were repeated with various initial pressures.

RESULTS AND DISCUSSION

The earlier studies included those at very low surface pressures, necessitating high performance liquid chromatography (HPLC) analysis of the monolayer material after collecting and extracting it. However, for moderately and highly compressed monolayers, the kinetics can also be followed by simply measuring the decrease in π as a function of time. This is because in the moderate to high surface pressure range, π-area curve is linear[10], implying that π is proportional to surface concentration. Moreover the isotherm is steep, which means that the concentration does not vary appreciably even for a relatively large drop in the surface pressure. Thus the surface concentration can be taken as constant during the course of the experiment. This procedure, however, is not valid for studying reactions in an expanded monolayer or monolayers at low surface pressures, region where the isotherm is neither linear nor steep. That implies that during a run, the variation in surface pressure is not sensitive to changes in surface concentration changes and consequently a measurement of π would not yield accurate information about the changes in surface concentration.

The experimental results bear out the validity of the assumption of the constant surface concentration for compressed monolayers. The surface pressure decreases as the reaction progresses and this decrease is linear in time, except for an initial non-linearity in case of highly compressed films attributable to a relaxation of the monolayer after it has just been compressed. A blank run on water without the oxidant as the sub-phase showed this decrease, without the subsequent linear decrease.

The results, shown in Fig. 1, indicate the effect of varying the initial surface pressure on the rate of the reaction. It is found that at lower values of π, the slopes of the π-t curves are the same for a range of initial surface pressures. This implies that the rate of the reaction is the same in this range and does not vary with the initial surface pressure. At very large initial surface pressures (> 12 mNm[-1]), however, the reaction is considerably slower.

Approximately constant rate at intermediate initial surface pressures can be explained by the fact that the surface concentration corresponding to all values of π within the range is about the same-a consequence of the aforementioned steepness of the π-area isotherm.

At very high surface pressures, (*e.g.* > 12 mNm[-1]), the reaction is considerably slower. This was observed in the earlier study[9], which used HPLC to analyze the extracted reaction mixture. The low rate in highly compressed films is likely caused by two factors. In the compressed film, the preferred skew conformation of the

disulfide molecule is difficult to achieve, since the octadecyl chain cannot be oriented to give the conformation[10]. Also in the extremely compressed monolayer, the aqueous oxidant is expected to be squeezed out from the interfacial region, leading to a slower reaction.

The linear portion of each of the curves in Fig. 1 was least-squared fitted to get the values of the rate constant. The values are given in Table-1 and depicted in Fig. 2. While values 2 to 5 in the table (the higher four points in the figure) can be interpreted in terms of surface concentration since these readings correspond to linear portion of the force-area isotherm, value 1 (the lowest point in Fig. 2) cannot be interpreted thus, as π does not vary linearly with concentration in this region of the force-area isotherm.
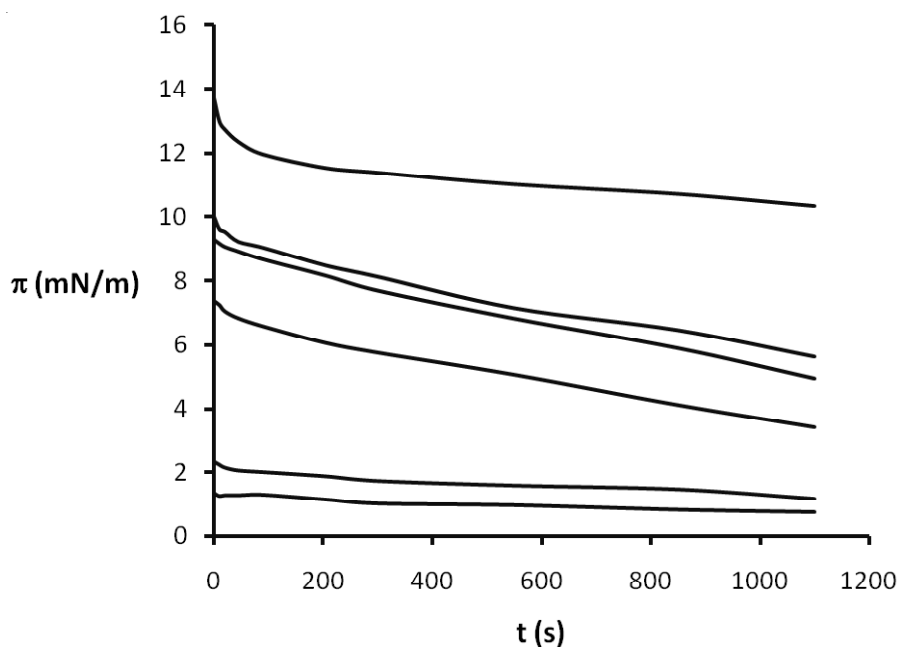

Fig. 1   Variation of surface pressure with time for films of 1-octadecanethiol over 1×10^{-4} $K_3Fe(CN)_6$ in 0.001 M HCl at 25 ºC at various initial surface pressures

TABLE-1
RATE CONSTANT AT VARIOUS INITIAL SURFACE PRESSURES

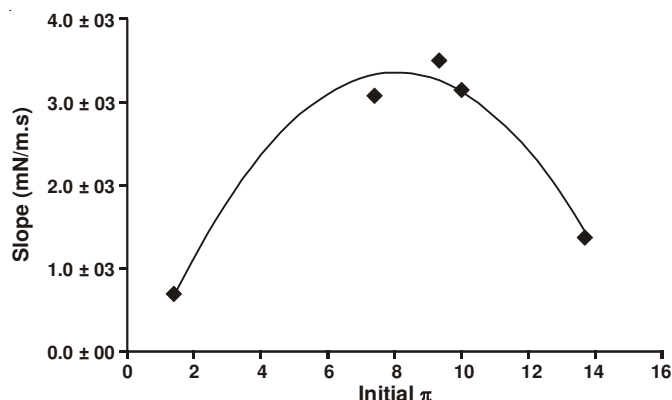|	π_o (mN/m)	k (mNm^{-1})/s
1	1.4	7.04×10^{-4}
2	7.4	3.08×10^{-3}
3	9.3	3.51×10^{-3}
4	10.0	3.14×10^{-3}
5	13.7	1.38×10^{-3}

Fig. 2.　Variation of the slope of the linear portion of π-t curves of Fig. 1 with π_o. For the higher initial surface pressure (the higher 4 points), the slope can be identified with the pseudo-zero order rate constant

Conclusion

This study has demonstrated that for the oxidation of compressed monolayer of 1-octadecanethiol leading to a surface-inactive product, the reaction can be followed by measuring changes in surface pressure with time. For intermediate values of the initial surface pressures, the rate constant varies in a relatively narrow range ($< \pm 7$ %). For extremely compressed monolayers, the rate constant decreases by up to 60 %. This has been interpreted in terms of a squeezing out of the sub-phase oxidant from the monolayer region as well as a less favourable orientation of the octadecyl side chains to form the preferred skew conformation of the disulfide product.

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REFERENCES

1.　A.E. Alexander and J.H. Schulman, *Proc. R. Soc. London, Ser. A*, **161**, 115 (1937).
2.　A.E. Alexander and E.K. Rideal, *Proc. R. Soc. London, Ser. A*, **163**, 60 (1937).
3.　J. Ahmad and K.B. Astin, *J. Am. Chem. Soc.*, **108**, 7434 (1986).
4.　J. Ahmad and K.B. Astin, *J. Am. Chem. Soc.*, **110**, 8175 (1988).
5.　S.J. Valenty, *J. Am. Chem. Soc.*, **101**, 1 (1979).
6.　J. Ahmad and K.B. Astin, *Langmuir*, **4**, 780 (1988).
7.　J. Ahmad and K.B. Astin, *Langmuir*, **6**, 1098 (1990).
8.　J. Ahmad and K.B. Astin, *Langmuir*, **6**, 1797 (1990).
9.　J. Ahmad and K.B. Astin, *Angew. Chem.; Int. Ed. Engl.*, **29**, 306 (1990).
10.　J. Ahmad and K.B. Astin, *Colloids Surf.*, **49**, 281 (1990).
11.　J. Ahmad, *Langmuir*, **12**, 963 (1996).
12.　J. Ahmad and N.D. Silavwe, *Asian J. Chem.*, **14**, 1282 (2002).
13.　J.K. Kumar and J.S. Oliver, *J. Am. Chem. Soc.*, **124**, 11307 (2002).
14.　J.S. Oliver and J. Singh, *J. Org. Chem.*, **62**, 6436 (1997).