

Trapping of molecules in alkanethiol self-assembled monolayer matrices

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Reactions of NH_4^+ in water solutions with self-assembled monolayer (SAM) surfaces result in the deposition of ammonia in the monolayers. Similarities between this and the soft landing of ions seen in low energy gas phase ion–surface collisions suggest that monolayers can be used as matrices to preserve species. Ammonia can be incorporated only into thicker SAMs such as those made from octadecanethiol. Reactions with larger ions do not lead to trapping. Trapped ammonia desorbs during prolonged exposure of the SAMs to vacuum.

1. Introduction

Low energy ion–surface collision [1] is one of the methods for inducing unusual reactions between an incoming gas phase ion and an organic species bound to the surface. These tandem mass spectrometric studies have been carried out most extensively with self-assembled monolayers (SAMs) [2]. The principal process occurring during the collision is the transfer of the ion kinetic energy to the internal energies of the colliding partners which are manifested in the fragmentation of the ion or the reaction of the ion or its fragments with a surface bound species [1]. Since the centre of mass collision energies in these experiments are comparable with bond energies, the process can be used very effectively in breaking (by a process called surface induced dissociation) or making of chemical bonds (referred to as ion–surface reactions). In ion–surface reactions [3], a process of particular interest to this work, a mass selected ion is made to collide with a surface at a desired collision energy, generally of the order of a few tens of eV, and the scattered-ion mass spectrum is analysed. A large number of ions undergo reactions at the surface; the most intensely researched are the hydrogen and fluorine atom pick-up reactions [1]. The collisions also lead to chemical modification of the surface (see [1] for a detailed discussion). Low energy ions are extremely surface sensitive and spatial control of the transformations is possible. For this reason, the method has direct technological relevance. Of the several processes discovered so far, the trans-halogenation reaction leading to chlorine for fluorine exchange reactions at fluorocarbon self-assembled monolayer surfaces [4, 5] and

soft landing of ions in fluorocarbon matrices [6] are particularly noteworthy. Soft landing of ions is one of the most effective ways of providing controlled chemical transformations which could be important in optoelectronics, catalysis, electrochemistry and related areas. This paper reports an experiment used to soft land molecules in self-assembled monolayer matrices by reacting them with ions in electrolytic solutions.

2. Experimental

All the monolayers were prepared by standard literature procedure [2]. Briefly, a 1000 Å thick gold film deposited on a polished glass slide was dipped in a 1 mM solution of the thiol in ethanol for about 12 h. The monolayer prepared in this way was washed with absolute ethanol and water in that order and used for the reaction. It was then dipped in a 2 mM solution of NH_4Cl in water and a current of 1 mA at 1 V was passed through the solution, keeping the SAM as cathode and a graphite rod as anode. After a minute, the SAM surface was withdrawn from the solution and was washed repeatedly with water and absolute ethanol in that order. The sample was immediately introduced into the ultra high vacuum chamber of the X-ray photoelectron (XPS) spectrometer for analysis. The non-monochromatic $\text{MgK}\alpha$ induced X-ray photoelectron spectrum was acquired with a VGESCA LAB MkII spectrometer working at a base pressure of 1×10^{-9} Torr. The X-ray flux was kept at 80 W to avoid surface damage during the measurement. No change in the spectrometer vacuum was observed during measurements at room temperature. For the high temperature measurements, the SAM was mounted

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on a heatable stub and the temperature was varied by resistive heating. All the spectra were averages of 20 scans. The spectrometer was operated at pass energies in the range 20–100 eV. The binding energies are referenced to the Au 4f_{7/2} peak at 84.0 eV.

3. Results and analysis

The use of XPS in the characterization of SAMs is well documented [7–10]. A typical photoelectron spectrum of the monolayer shows features due to the alkanethiol and the underlying gold. Within the detection limit of XPS, contaminants were not detected. The XPS spectrum of the reacted SAM shows the appearance of a single peak in the N 1s region (figure 1). A binding energy of 399.0 eV is observed for aliphatic amines, adsorbed ammonia, etc. [11]. This peak disappears completely for samples kept in a vacuum for more than a few days. It also does not show up for samples stored in the laboratory for a couple of days and introduced into the vacuum chamber later. The sample shows a peak at 532.0 eV binding energy (BE) due to reaction of the ionized SAM with the solvent that is present even after prolonged exposure to vacuum [12]. The S 2p signal remains at 162.5 eV, just as in the original monolayer, indicative of the Au⁺S⁻ thiolate char-

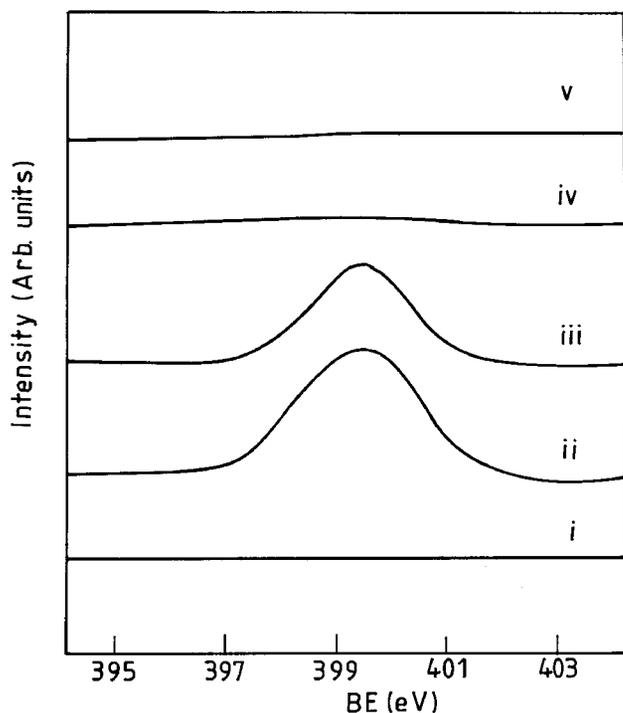


Figure 1. N 1s region of the X-ray photoelectron spectra of (i) octadecanethiol SAM before reaction, (ii) octadecane-, (iii) dodecane-, (iv) octane- and (v) butanethiol SAMs after reaction with NH₄⁺ in water. Note that N 1s intensity is seen only in octadecane and dodecane SAMs after the reaction.

acteristic of the SAM [7, 8] (figure 2). Temperature dependent measurements show that the N 1s signal disappears before the desorption temperature of the SAM (around 150°C), thereafter no N 1s peak is seen. No N 1s intensity is seen upon cooling the surface back to room temperature or for a SAM just dipped in NH₄Cl solution, showing that the N 1s peak is not due to physisorption or due to deposition of ammonium ions from solution or due to contamination from the vacuum chamber. It may be noted that SAMs have very little surface energy, and adsorption on them does not occur as with a bare Au surface [10]. No change in any region of the SAM was seen upon exposure to anions and there was no emergence of new peaks.

Experiments were performed in which the chain length of the SAM was varied. In these studies involving butane-, octane-, dodecane- and octadecanethiol SAMs, the N 1s intensity was found only in octadecane and dodecane SAMs (figure 1). No N 1s intensity was observed for reactions with solutions of tetramethyl, tetraethyl and tetrabutyl ammonium ions. However, a new peak at 532 eV is observed in all the cases. Reaction with triphenyl phosphonium ion did not show any phosphorus intensity. Both of these suggest the importance of the size of the ions in the observed reactions, a

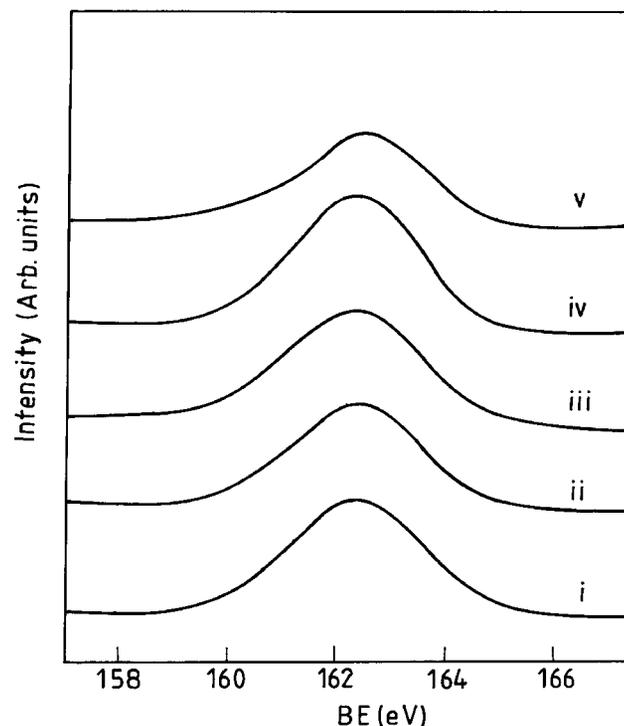


Figure 2. The S 2p region of (i) octadecanethiol SAM before reaction, (ii) octadecane-, (iii) dodecane-, (iv) octane- and (v) butanethiol SAMs after reaction with NH₄⁺ in water. There is no observable change in the intensity or peak shape between the spectra.

conclusion supported by gas phase soft landing experiments [6].

The above results suggest that nitrogenous species can be deposited at the hydrocarbon surface as a result of reaction with ions in solution. The fact that the peak disappears upon prolonged exposure to vacuum and upon exposure to the atmosphere for a few days supports the suggestion that this is due to deposition of NH_3 in the SAM matrix. The disappearance of N 1s during heating also supports the same conclusion. Additional support for the foregoing comes from the surface coverage, which is estimated to be 2×10^{14} atoms cm^{-2} , corresponding to less than approximately one nitrogen atom per alkyl chain, assuming a near neighbour distance of 7 Å between the alkyl chains [13]. This estimate was made by taking the N 1s to S 2p atomic cross-section ratio to be 1.24 and the attenuation of S 2p intensity due to the overlayer to be 30%. An attenuation length of 80 Å for the S 2p photoelectrons [14] and a SAM thickness of 25 Å was assumed. In a separate experiment in which an increased exposure time was employed, no increased N 1s intensity was observed, indicating saturated coverage, which again supports soft landing. A larger deposition density may not be possible since the ion is approaching the surface with thermal energy, and deeper penetration is unlikely. Electrochemical experiments on SAMs also suggest that ion penetration is negligible [15].

It is proposed that the ion approaching the SAM surface undergoes electron transfer with the alkyl chain [1]. Electron transfer at the SAM–electrolyte interface has been researched intensively in the recent past [16]. The general belief is that tunnelling from the surface is the most probable pathway, although involvement of the adlayer is important. The soft landing experiment reported here may occur via electron transfer, which is one of the possible mechanisms reported in the gas phase ion–surface reactions [1]. Upon ion–surface encounter in the gas phase, electron transfer from the surface leads to the formation of an ionized surface (alkyl chain in the case of a SAM), which can undergo fragmentation subsequently. The fragmented surface species may react with the neutralized projectile (due to electron transfer from the surface) or its fragments, leading to ion–surface reaction products in the gas phase while the radical at the surface can react with the neutralized ion or its fragment leading to a chemically modified surface. While electron transfer occurs in this process, there is also another ion–surface reaction channel without electron transfer in which the reaction occurs via a concerted pathway [3]. It is important to mention also that the ion–surface reaction mechanism and surface modification outlined above can be a single-step event without involving charge separation [1]. It has

been shown that the ion–surface encounter leads to deposition of ions and neutrals at the SAM [17]. In cases where deposition is observed, there have been reports of an ion–surface reaction. Upon ion–surface interaction in the electrolytic solution, electron transfer can lead to ionized organic species, and a reaction between the neutralized ion and the ionized surface can occur just as in the case of a gas phase ion–surface collision; however, momentum transfer leading to fragmentation is not a critical event. It is important to note that the neutralized projectile can get buried in the SAM matrix just as reported earlier [6, 17], and the N 1s signal is attributed to this. The ionized organic surface species can become neutralized subsequently, as electron transport exists between the underlying substrate and the organic chain. Longer monolayers may only permit this entrapment since the monolayer assembly is more complete in them and therefore we see no N 1s in lower SAMs. The entrapment is feasible only if the ion size is small, and we do not see this phenomenon with triphenylphosphonium and tetramethylammonium ions. Electron transfer can occur over a larger distance, and there is also an opportunity for the ion at the surface to react with the solvent molecule because of both their large concentration and their proximity to the surface. In fact this does happen, and this is attributed to the cause of the O 1s intensity [12].

Trapping species in inert matrices is the central process in all the various forms of matrix isolation spectroscopy. The principal difference between this and the experiment here is that the matrix is a monolayer of a few tens of angstroms in thickness. Since the deposition is effected in solution, it is likely that the trapping is confined to the very top of the surface. Therefore, the trapped species form much less than a monolayer in surface coverage. Diffusion of these species within the monolayer will be an interesting theme of investigation. It may be noted that in low energy ion–surface collision. It was shown that I^+ can be deposited in fluorocarbon monolayers, and subsequent reactions confirmed the presence of I_2 in the surface, indicating motion of ions in the matrix and reactions between them [17].

4. Conclusion

This experiment has demonstrated the use of monolayers as matrices for solution phase experiments. The study also supports the proposition of electron transfer in ion–S surface interaction. The results presented here imply that it is possible to avoid sophisticated methods such as mass selected low energy ion–surface collisions to trap species in molecular surfaces, at least in certain instances. The spectroscopy of such trapped species will be interesting, although difficult owing to the low concentration of the species concerned. Monolayers with

greater thicknesses may be important to increase the concentration of the trapped species. Such experiments conducted in reactive matrices can be used in effecting chemical transformations of monolayers. Experiments are currently underway along these lines.

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