

Kinetics of alkanethiol monolayer desorption from gold in air

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Thermal desorption of an alkanethiol monolayer from a gold substrate into a gaseous medium under ambient pressure was investigated using XPS and it was found that there exist 2 consecutive 1st order kinetics mechanisms with activation energies of 29.9 and 32.7 kcal mol⁻¹, respectively, *i.e.* on average ~15% higher than reports for liquid media desorption.

Alkanethiol molecules can adsorb on a gold surface through gold–sulfur bonding and self-assemble into an ordered structure at the molecular scale called a self-assembled monolayer (SAM). For modelling purposes, of our recently developed “direct laser patterning” (DLP) methodology for SAMs,¹ we are interested in desorption kinetics of SAMs in air. To calculate the feature sizes generated using DLP one needs to combine the SAM desorption kinetics equation with the heat diffusion equation.² Accurate activation energy values will allow for correct prediction of pattern sizes generated in DLP, *i.e.* a thermally driven process. Such kinetics information is also useful for many other applications of SAMs (see ref. 3 and references therein).

Thermal stability and kinetics of SAM desorption in solvents have been investigated using ellipsometry^{3,4} and temperature programmed desorption.⁵ The coverage of SAMs in this study was characterized through X-ray photoelectron spectroscopy (XPS), which is significantly better than ellipsometry and wetting observation used in previous studies for quantitative analysis.

Gold films supported on microscope glass slides were used as substrates for making SAM surfaces.¹ Thermal desorption of 1-hexadecanethiol (HDT) in air, in an oven, was studied for temperatures ranging from 383 to 653 K.† The samples were kept under 97% nitrogen and analyzed using XPS (Axis-165, Kratos Analytical) in less than 24 hours.‡ The ratio of areas of the S2p doublet over the Au4f peak was calculated and then normalized with respect to that of unheated samples to find monolayer coverage (average value from 6 unheated samples was used for normalization).

The XPS spectra of heated samples show evidence of SAM desorption. For example, the 162 eV S2p doublet signal (*i.e.* S2p_{3/2} and S2p_{1/2} with 2:1 ratio of photo-ionization cross sections and 1.2 eV difference in binding energy), indicating chemisorbed sulfur, was quantitatively less intense than those collected from SAMs at full coverage (unheated samples) under the same conditions (see Fig. 1). The S2p region of XPS spectra shown in Fig. 1 clearly demonstrate the loss of sulfur from the gold surface after heating the sample at 653 K for 1 minute. The C1s region of the same samples also corroborated the desorption of SAMs through loss of

the carbon signal (data not shown). The XPS results were consistent with our wetting observations; all samples appeared hydrophobic prior to heating whereas after heating samples that experienced higher temperatures for longer times were visibly hydrophilic. Omitting the thorough rinsing step after heating† sometimes caused a weak shift in sulfur peaks; such shifts of S2p peaks are known to signify the presence of physisorbed sulfur.

Fig. 2 shows the time-dependent desorption of HDT SAMs at different temperatures in air. The SAM desorption rate was slower than those from earlier studies of similar SAMs into solvent media at 383 K reported in refs. 3 and 4 for HDT and 1-heptadecanethiol, respectively (there is evidence in the literature^{6,7} that for long chain alkanethiols kinetic constants do not change). At high temperatures the SAM is completely desorbed in a few minutes (Fig. 2a). The time for desorption of 50% of an HDT SAM in decalin at 383 K is less than 2.5 min³ and that of a 1-heptadecanethiol SAM under the same conditions is less than 1 min;⁴ it takes, however, ~1 hour to desorb 50% of HDT in air (Fig. 2b).

At 383 K full desorption was not achieved during our test period, *i.e.* 2 hours. The desorption profile at 383 K seemingly has a horizontal asymptote at higher than zero coverage (dashed line in Fig. 2b), at ~40% coverage. Thermal desorption at 363 K also showed the same trend as that at 383 K with a higher asymptote (data not shown). Shon and Lee⁴ reported such an asymptotic desorption behavior near 20% SAM coverage for desorption of 1-heptadecanethiol in decalin at a similar temperature (*i.e.* 373 K); whereas Garg *et al.*³ did not report any asymptotic behavior for desorption of HDT in decalin. Asymptotic behavior can signify that the thermodynamic yield of the SAM desorption reaction is not 100% below a certain temperature threshold, which is characteristic of endothermic reactions. Shon and Lee⁴ reported full desorption at 383 K in 3 min; but they could not reach full

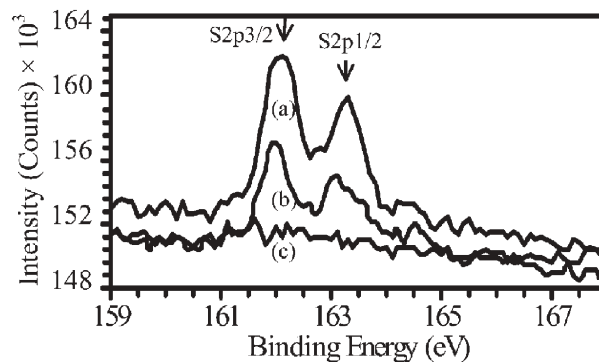


Fig. 1 High resolution XPS spectra for S2p of HDT SAM on gold. (a) Before heating, (b) after heating at 383 K for 2 hours and (c) after heating at 653 K for 1 minute.

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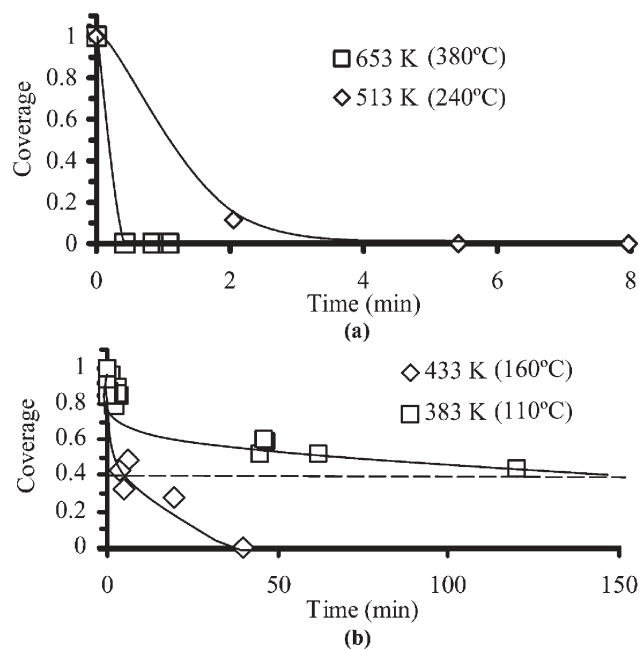


Fig. 2 Thermal desorption profiles of HDT SAMs from a gold surface at (a) 653 K (=380 °C) and 513 K (=240 °C), (b) 433 K (=160 °C) and 383 K (=110 °C). The lines are to guide eyes.

SAM desorption at 363 K and 343 K, even after 4 hours. Thus, for long chain alkanethiol SAMs the thermodynamic threshold for incomplete desorption is between 363K and 383 K; whereas the same threshold for desorption in air is between 383 K and 433 K (Fig. 2b). The lower threshold of incomplete desorption in liquid shows that, thermodynamically, the desorption reaction is more productive in liquid media, which could be explained in terms of solvation of desorption products, *i.e.* dithiols, in liquid media. Furthermore, stronger interaction of solvent with the SAM results in swelling and disorder, which in turn leads to faster desorption at a fixed temperature.⁵ All monolayers were desorbed in shorter time scales at higher temperatures. The downward shift of the ultimate desorption asymptotic line with increasing temperature shows thermodynamic enhancement of the yield of the SAM desorption reaction. This is consistent with what is expected from endothermic reactions. Such dependence of the final yield of a desorption reaction has previously been reported for desorption in solvent media as well.^{3,4}

The data in Fig. 2 illustrate an important feature of the desorption behavior of the SAMs. Comparing the slopes of the desorption profiles (rate constants) with increasing temperature, the rate constant will also increase. Based on qualitative observations a two consecutive first order regime is suggested in the literature for the desorption of SAMs in liquid media.³ In this study we provide a quantitative analysis and model for the desorption of SAMs. But before that, to determine the order of the desorption kinetics, the data in Fig. 2 were analyzed with the classical graphical tests: the graphs in Fig. 2 are not linear, therefore, the SAM desorption reaction in air cannot be a zeroth order reaction. Semilogarithmic plots of data were used to see if the reaction follows first order kinetics, *i.e.* the rate of desorption is proportional to the surface concentration of the SAM. The analysis showed that experiments at higher temperatures follow a

linear trend more closely than those at lower temperatures (linear correlation: $R^2 = 0.9$ at 653 K and 513 K, but 0.7 and 0.4 at 433 and 383 K, respectively). We also examined the possibility of a second order desorption, *i.e.* the rate of desorption is proportional to the square of the surface concentration of the SAM. A linear relationship between the inverse of products *versus* time is characteristic of a second order reaction. The linear correlation at higher temperatures was poor ($R^2 = 0.6, 0.7, 0.4$ and 0.8 at 653 K, 513 K, 433 K and 383 K, respectively). We concluded that desorption in air should be represented by a first order reaction.

First we examined the case of a single first order kinetics mechanism to describe the desorption. The data from *all* examined temperatures were fitted to the first order kinetics equation using the least square method and the activation energy was back calculated through error minimization. Thus, the resulting desorption profiles were fitted to the following equation:

$$dC/dt = -k(T)C \quad (1)$$

where C denotes the surface concentration of the SAM, and k is the rate constant. The rate constant is a temperature (T) enhanced factor according to the Eyring equation:⁸

$$k(T) = \frac{k_B T}{h} \exp\left(-\frac{\Delta G}{RT}\right) \quad (2)$$

where k_B is the Boltzmann constant, h is Planck's constant, ΔG is the Gibbs free energy of activation for the desorption reaction, and R is the universal gas constant.

The temperature-dependence of k is determined according to eqn (2) for a known value of ΔG . To find the final SAM concentration on a surface, the desorption rate [eqn (1)] was integrated over time to give:

$$C(T,t) = C_0 \exp\left(-\frac{k_B T t}{h} \exp\left(-\frac{\Delta G}{RT}\right)\right) \quad (3)$$

where C_0 represents the initial SAM coverage, which is assumed to be complete and uniform everywhere (*i.e.* $C_0 = 1$). The least square method was used to fit eqn (3) to experimental results. The error function was calculated for a wide span of ΔG values (0–90 kcal mol⁻¹) to identify the minimum.

The activation Gibbs energy was calculated to be 30.5 kcal mol⁻¹, which is close to previously reported data in the literature for long chain alkanethiol SAMs, *i.e.* 30.1 ± 0.5 kcal mol⁻¹.⁶ We verified that elimination of data points from any of the tested temperatures would not change the final calculated activation Gibbs energy by more than ±0.4 kcal mol⁻¹. This value is shown to be fairly constant for alkanethiols of different chain lengths^{3,6} and terminal groups.⁷ This independence is attributed to the fact that chemisorption occurs through interaction of the sulfur atom with the gold surface and the rest of the molecule does not play a significant role.⁷

The calculated ΔG , *i.e.* 30.5 kcal mol⁻¹, is higher by 15% compared to the value previously reported for desorption of the same SAM into liquid solvent, *i.e.* 27 kcal mol⁻¹.³ This is consistent with our observation of the slower desorption of SAMs from gold in a gaseous medium compared to a solvent medium. The observation also conforms to theoretical expectations that solvation interactions of molecules are stronger in a solvent

medium compared to a gaseous medium where molecules are far apart. Stronger solvation interactions of media molecules both thermodynamically and kinetically are in favor of faster desorption in solvent. Thermodynamically HDT, with a bulk vapor pressure of 0.1 mmHg at 293 K and a bulk boiling point of 303 K, does not volatilize at ambient temperatures into gaseous medium but it can easily be dissolved in organic solvents. This argument shows that desorption of HDT should lead to a thermodynamically more stable state in a solvent medium compared to a gaseous medium. Thus, it can be expected that the transition state that leads to the final desorption products will also be more stable in solvent, and kinetically more favorable with a smaller ΔG value.

Schlenoff *et al.*⁵ considered a number of mechanisms and concluded that SAM desorption (in solvent) does not generally follow single first or second order kinetics. They suggested superposition of several desorption rates corresponding to a range of binding site energies. A two consecutive first order kinetics regime was suggested³ for desorption of SAMs in solvents: an initial fast desorption regime (mainly from sites of weak Au-S bonding, *e.g.* defects, grain boundaries where SAM is poorly ordered) followed by a slow regime. In the slow regime remaining thiol molecules (mainly in highly ordered regions) either desorb directly or migrate to weak bond sites as the result of thermal treatment⁹ (both slow). Thus, the kinetics of desorption from weak bond sites dominates in the first regime whereas the collective kinetics of direct desorption from strong bond sites and migration to weak bond sites (as rate limiting step) dominates in the slow regime. The same conclusion is reached regarding the kinetics of thermal desorption and exchange of SAMs in various studies in liquids.^{3–5,9,10} Garg *et al.*³ did not, however, mention any transition time for shifting from the fast to the slow regime. We examined this idea quantitatively to see if it can better describe our results and open the door to a more quantitative evaluation of the suggested mechanism. We assumed a fixed temporal threshold for transition between the two first order kinetics (t_c). Such an assumption will allow us to estimate, over the range of temperatures examined, how long desorption of weakly bonded molecules will take. The t_c in principal could be a temperature-enhanced value but here (for simplicity and as first approximation) is assumed to be a constant. Fitting the experimental data points to such a two regime mechanism required a 3 parameter least square optimization (a ΔG value for each regime and t_c). By iteratively fixing one of the three parameters and finding the other two through graphical minimization of error function, after 4 iterations we found: $\Delta G_{\text{fast}} = 29.9 \text{ kcal mol}^{-1}$, $\Delta G_{\text{slow}} = 32.7 \text{ kcal mol}^{-1}$, and $t_c = 87 \text{ s}$. The result was reconfirmed through calculating the error function on a grid with all 3 parameters changing: 0.1 kcal mol⁻¹ spacings for activation energy and 1 second steps for transition time. The optimal result conformed with findings using the iterative method. This transition time (*i.e.* 87 s) can be considered as the temporal upper limit for dominance of the first desorption regime given that there might be an enhancement with temperature for switching from fast to slow regime. Fig. 3 shows the significance of the 2 step mechanism by providing a better fit to the experimental data, especially for longer time periods.

To further verify the above value for t_c , we fitted the data for the first 87 s of individual series of experiments (fixed temperature) to Eyring's equation; the resulting values for ΔG_{fast} were all in

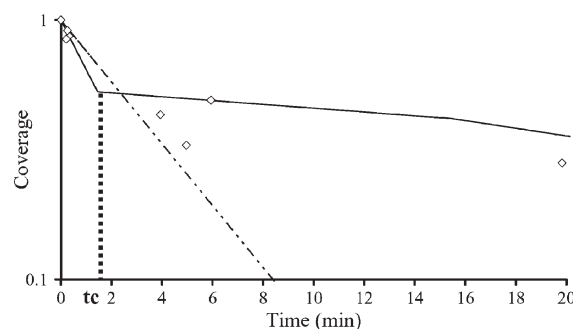


Fig. 3 Desorption kinetics for HDT at 433 K (160 °C). Solid line represents 2 step desorption kinetics; the dashed-dotted line represents a single step kinetics mechanism. Symbols are experimental data points.

range of 28–34 kcal mol⁻¹ with averages within less than 4% of that obtained from the first method. The same test on ΔG_{slow} also resulted in values in the range of 30–35 kcal mol⁻¹ with averages close to the reported value above (less than 4% difference). The agreement further confirms the transition threshold time.

We used the results of the above kinetics investigation in our thermokinetics model² for DLP. Since laser patterning occurs in a few seconds,¹ the energetics of the fast desorption regime were used for calculations. The SAM coverage profiles were examined at powers of 73, 49, and 24 mW. Slower rates of desorption of SAMs in air cause line widths (full SAM desorption) produced in DLP to decrease by ~20%. The new data helps in better predicting DLP outcome as a result of the more accurate kinetics information available due to this study.

Notes and references

† The samples were rinsed with ethanol and blown dry with nitrogen prior to the experiments. The samples were placed in a preheated oven at the desired constant temperature (accuracy $\pm 2 \text{ K}$).

‡ XPS operating conditions: base pressure $0.5 \times 10^{-10} \text{ Torr}$; X-ray source, aluminium (monochromatized), initial photon energy 1486.71 eV, operating power 210 W. Survey spectra pass energy 160 eV; binding energy range 0–1100 eV, steps of 0.33 eV. We examined high-resolution spectra of O1s, C1s, S2p and Au4f regions for each sample (pass energy 20 eV, steps of 0.1 eV). In data processing, the intrinsic relative sensitivity factors and transmission function of the instrument were used. For composition analysis peak areas were integrated, with linear background subtracted. XPS signal of SAMs on gold surfaces depends on take-off angle.

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