Oxygen Attachment on Alkanethiolate SAMs Induced by Low-Energy Electron Irradiation

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Abstract

Reactions of $^{18}\text{O}_2$ with self-assembled monolayer (SAM) films of 1-dodecanethiol, 1-octadecanethiol, 1-butanethiol, and benzyl mercaptan chemisorbed on gold, were studied by the electron stimulated desorption (ESD) of anionic fragments over the incident electron energy range 2–20 eV. Dosing the SAMs with $^{18}\text{O}_2$ at 50 K, results in the ESD of $^{18}\text{O}^-$ and $^{18}\text{OH}^-$. Electron irradiation of samples prior to $^{18}\text{O}_2$ deposition demonstrates that intensity of subsequent $^{18}\text{O}^-$ and $^{18}\text{OH}^-$ desorption signals increase with electron fluence and that absent electron pre-irradiation, no $^{18}\text{O}^-$ and $^{18}\text{OH}^-$ ESD signals are observed, since oxygen is unable to bind to the SAMs. A minimum incident electron energy of 6–7 eV is required to initiate the binding of $^{18}\text{O}_2$ to the SAMs. O_2 binding is proposed to proceed by the formation of $\text{CH}_{x-1}^\bullet$ radicals via resonant dissociative electron attachment and non-resonant C–H dissociation processes. The weaker signals of $^{18}\text{O}^-$ and $^{18}\text{OH}^-$ from short-chain SAMs are related to the latter's resistance to electron induced damage, due to the charge-image dipole quenching and electron delocalization. Comparison between the present results and those for DNA oligonucleotides self-assembled on Au [Mirsaleh-Kohan, N. et al. *J. Chem. Phys.* **2012**, *136*, 235104] indicates that the oxygen binding mechanism is common to both systems.

1. INTRODUCTION

Self-assembled monolayers (SAMs) are widely used in many areas of research and are of considerable fundamental and practical interest.^{1–3} The properties of SAMs (i.e., low thickness, densely packed, ordered stacking, high stability, choice of functional heading groups, and resistance against chemicals)^{2,4} make these surface coatings suitable for varied applications including control of wetting and adhesion,^{5,6} biosensors,⁷ microcontact printing,⁸ and cell adhesion.² Furthermore, these molecular assemblies present interesting structural and physicochemical properties (i.e., small thickness of about 1–3 nm and the molecular size of its structural elements) for radiation-induced nanostructure patterning lithography.^{1,3} High-resolution patterning (0.5–1 nm scale) on SAMs with electron beams is particularly interesting for microelectronics and nanolithography. Such patterning is possible by focusing adequately the electron beam.⁹ SAMs of *n*-alkanethiols and phenylthiols have been particularly useful for radiation-induced patterning, because of the close packing and

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ordering of the molecules of the SAM.^{10,11} For these reasons, alkanethiolate monolayers are considered the most promising resists for SAM-based lithography.¹²

Interest in the use of low-energy electrons (LEEs) to chemically modify SAMs is in part related to a potential improvement in the spatial resolution for electron beam patterning. High-energy electrons (e.g., $E > 1$ keV), as they impact the substrate, produce large quantities of secondary LEEs which possess energies within a distribution lying mostly below 20 eV.⁴ The interactions of these secondary electrons, in addition to the multiple electron scattering effects, limit the spatial resolution obtainable with high energy electrons by broadening the effective area of irradiation.^{4,13} Such problems can be minimized when using low-energy beams by irradiation through a mask^{14,15} or by tunneling LEEs from the tip of a scanning tunnel microscope (STM) into the SAM, to induce specific reactions at different positions on the surface.^{16,17} Effectively, another potential advantage of SAM modification by LEE irradiation is the selectivity of damage by the precise control of the incident electron energy (E_i). It has already been established that LEE (1–50 eV) impact induces chemical modification in hydrocarbon SAMs.^{4,12,18,19} Cleavage of C–C, Au–S, C–S and C–H bonds occurs, although the latter process seems the most important.^{4,12,18} For E_i near 10 eV, the cross section for C–H dissociation is at a maximum due to dissociative electron attachment (DEA), and this permits an effective but ‘gentle’ modification of the chemical structure of the SAM by promoting loss of hydrogen.¹⁸ Dehydrogenation can cause for *n*-alkanethiolate aliphatic SAMs, a loss of structure in the film by formation of C=C bonds, irregular cross-linking, or reduction of film thickness.^{1,12} In the case of aromatic SAMs, cross-linking can happen after dehydrogenation.¹⁴ On either case, SAMs are advantageous for lithographic patterning by LEE irradiation as positive or negative resist.¹ Furthermore, the possibility of functionalizing SAMs by LEE irradiation was demonstrated by Hamman et al.²⁰ The authors incorporated nitrogen-containing groups on 10-undecene-1-thiol SAM chemisorbed on Au by depositing overlayers of NH₃ and subsequent exposing the resulting film to 15 eV electrons. Such modification could permit the chemical grafting of various molecules, like DNA, proteins or drugs,^{21,22} onto a patterned, chemically modified surface.

The present work is concerned with the detailed investigation of LEE-driven mechanisms leading to the binding of O₂ onto LEE-irradiated *n*-alkanethiolate SAMs; it is a continuation of our earlier work on reactions of O₂ with thin films of irradiated DNA, observed by electron stimulated desorption (ESD).²³ As in lithography, the interactions of LEEs are thought relevant to a complete understanding of radiation damage to DNA since about 80% of the energy deposited into cells by ionizing radiation produces secondary electrons with energies lying mostly below 30 eV,^{24,25} with mean values near 10 eV (or lower, especially if the recently observed inter-molecular columbic explosion mechanism²⁶ has high probability). In radiobiology, it has long been known that exposure to high concentrations of O₂ increases the radiation damage.^{27,28} This enhancement or radio-sensitization is known as the “Oxygen Effect”, and has been attributed to reactions of molecular oxygen with damage sites formed within DNA. Enhanced damage was also recently observed by Alizadeh et al.²⁹ when irradiating plasmid DNA films with low energy photoelectrons under an oxygen atmosphere. The presence of O₂ was found to increase DNA strand break damage by a factor 2. Similarly, an “Oxygen Effect” was also identified in ESD measurements from DNA

oligomers dosed with O₂ at cryogenic temperatures;²³ enhanced desorption signals of O⁻ and OH⁻ were observed at elevated temperatures, but only from DNA films that had been exposed to LEEs. Thus it was shown that the observed enhanced desorption was due to an electron-induced process, and that O₂ can react with LEE induced damage sites in DNA.

This paper describing ESD measurements *n*-alkanethiolate SAMs dosed with ¹⁸O₂ has two objectives: first, to present an outline for a dry method to functionalize a surface with O₂ using LEE irradiation. With this technique, in contrast to plasma treatment, the SAM could remain largely undamaged. It would provide a means to keep such very thin molecular layers intact, while inducing chemical modification of the surface related to properties, such as wettability and adhesion,²⁰ for various applications. Secondly, this work would allow a better understanding of the previously observed ESD enhancement in O⁻ and OH⁻ desorption from DNA exposed to O₂,²³ by a comparison of the results and the related phenomena from *n*-alkanes and DNA.

2. EXPERIMENTAL SECTION

2.1. Preparation of *n*-Alkanethiolate Self-Assembled Monolayers (SAMs)

The Au(111)/glass substrates were purchased from ArrandeeTM (Germany) and consist of a ~0.7 mm thick borosilicate glass base coated with 2.5 nm of Cr, over which 250 nm of Au are deposited by vaporization. Prior to deposition of the alkanethiolate SAMs, the Au substrates were cleaned in a Piranha solution (70:30 v/v of H₂SO₄:H₂O₂) followed by ozone/UV treatment.^{20,30} Both treatments lasted 30 min. After each cleaning step, the Au substrates were rinsed with Millipore ultra-pure water (*R* > 18 MΩ) and dried with pressurized nitrogen. The cleaned substrates were subsequently immersed in ~1 mM solutions of the desired thiol in spectral-grade methanol. After immersion for 24 h, the SAMs were removed from the thiol solution, rinsed with methanol and dried with pressurized N₂. Four thiolate products from Sigma-Aldrich were used for the study: 1-octadecanethiol (ODT: CH₃(CH₂)₁₇SH), 1-dodecanethiol (DDT: CH₃(CH₂)₁₁SH), 1-butanethiol (BT: CH₃(CH₂)₃SH), and benzyl mercaptan (BM: (C₆H₅)CH₂SH).

2.2. Electron Stimulated Desorption System

ESD experiments were performed using a Time-of-Flight (TOF) mass spectrometer (Kore-5000 Reflectron TOF analyzer) in an UHV system reaching a base pressure of 5×10⁻¹⁰ Torr. A complete description of the instrument and its operation are given elsewhere.³¹ Briefly, each SAM sample was bombarded by a pulsed LEE beam from a Kimball Physics ELG-2 gun. The current of ~4 nA consisted of 800 ns pulses with a repetition of 5 kHz; it was incident at an angle of 45° with respect to the sample normal. The energy could be varied from 0.1 to 20 eV. A negative potential pulse (-2.4 kV, pulse width of 2 ms) was applied to the substrate immediately after the end of an electron pulse. The applied potential injected anions from the sample region into the entrance optics of the TOF mass analyzer positioned along the sample surface normal. Ion desorption yields measured as a function of electron energy are termed *yield functions*; they were measured from 2 to 20 eV (nominal values obtained prior to energy calibration) with electron energy increments of 0.5 eV and 50 000 electron pulses per point. On occasion, the total counts recorded in a

yield function are summed together to obtain a measure of the total anion desorption across a chosen energy range. Such data points are termed *integrated yield functions*.

Samples were introduced into the UHV system via a custom-built load-lock, and were attached to a closed-cycle He cryostat. The temperature of the samples was controlled with a resistive heating element, permitting a variation of the temperature between 20 and 300 K. Samples were degassed in the lock-lock chamber for at least 12 hours prior to their transfer into the TOF chamber for the experiments. For these experiments, irrespective of sample temperature, exposure to oxygen is expressed in monolayers (ML) of O₂, where 1 ML is that quantity of O₂ required to form a ML of O₂ on a Pt substrate at 20 K. This quantity has been determined to within 30% by a volumetric dosing procedure.³² From consideration of the molar volume of liquid O₂,³³ one ML of O₂ contains $\sim 10^{15}$ molecules·cm⁻². After recalibration, the quantity of O₂ needed to form a ML of O₂ was twice the quantity mentioned in one of our previous paper.²³ To simplify experimental analysis and to avoid confusion regarding the origins of detected desorption signals, dosing experiments were performed using ¹⁸O₂.

3. RESULTS

Prior to the deposition of ¹⁸O₂, the principal mass measured during ESD from *n*-alkanethiolate SAMs (i.e., 1-octadecanethiol (ODT), 1-dodecanethiol (DDT), and 1-butanethiol (BT)) was H⁻ (1 amu). Other masses (CH₂⁻ (14 amu) and CH₃⁻ (15 amu)) were detected, but in very low proportions in comparison with H⁻. These results are similar to those previously reported for aliphatic hydrocarbon thin films.^{18,34} In contrast, SAMs of benzyl mercaptan (BM) only exhibited H⁻ desorption, a result consistent with the observation that aromatic thiol SAMs are less damaged by irradiation.⁹ The response of SAMs under LEE irradiation was estimated by measuring the H⁻ ESD signal of neat SAMs (Figure 1). Two features were observed: the structures centered between 8.5 and 9.5 eV are associated with dissociative electron attachment (DEA: $\text{RH} + \text{e}^- \rightarrow (\text{RH})^{*-} \rightarrow \text{R}^\bullet + \text{H}^-$), while the monotonic increase at higher energies is attributed to dipolar dissociation (DD: $\text{RH} + \text{e}^- \rightarrow \text{R}^+ + \text{H}^- + \text{e}^-$). The DEA and DD processes, which are the only mechanisms known to produce anionic desorption below 70 eV, are well described in the literature.^{35–37} In general, as the length of the hydrocarbon (and therefore also the number of CH bonds) in the SAM increases, the H⁻ ESD increases as well. This trend is reversed however when going from DDT to ODT. This is somewhat surprising, as ODT is a longer molecule than DDT (a 18 C atom chain versus a 12 C atom chain) and hence forms a thicker SAM than DDT (about 30%).^{38,39} On the other hand, the nature (i.e., the length of the molecules) of the SAM can influence the molecular packing. It has been shown by STM that a lack of structure occurs for *n*-alkanethiolate (C_{*n*}H_{2*n*+2}) SAMs of 16 < *n* < 28 with even *n* values,^{10,40} decreases the packing of the SAM. This implies that the density of CH bonds decreases, plausibly explaining the lower intensity of H⁻ for ODT in comparison to DDT. At 50 K, the ESD measurements from pristine SAMs before exposure to ¹⁸O₂, shows no signal of ¹⁸O⁻ (18 amu) and ¹⁸OH⁻ (19 amu). After these ESD measurements (2–20 eV with a fluence of ~ 10 μC/cm² at an incident current of ~ 4 nA), exposure of the irradiated SAMs to 0.375 ML of ¹⁸O₂ at 50 K did not alter the yield functions of H⁻, CH₂⁻ and CH₃⁻. However for each of the studied SAMs, a major difference in ESD was the appearance of ¹⁸O⁻ and

$^{18}\text{OH}^-$ signals, both of which presented with a resonant DEA-type structure and DD signal at higher energies. Both signals increased with subsequent exposure to $^{18}\text{O}_2$ up to a total of 1.75 ML (Figure 2 for the case of DDT). The energy of the $^{18}\text{O}^-$ DEA maximum (at ~ 6.7 eV) is about 1 eV below that for the $^{18}\text{OH}^-$ (~ 7.7 eV).

Figure 3 presents integrated (from 2–20 eV) yield functions for $^{18}\text{O}^-$ or $^{18}\text{OH}^-$ ESD signals from SAM samples of varying composition. In each sequence of experiments for each SAM-type, ESD (2–20 eV, $\sim 10 \mu\text{C}/\text{cm}^2$) was measured from a pristine SAM sample at room temperature and again on the same sample, at 50 K (experiments 1 and 2 in Figure 3, respectively). No $^{18}\text{O}^-$ or $^{18}\text{OH}^-$ signals were detected. The SAM was then exposed to 0.375 ML of $^{18}\text{O}_2$. ESD measurements reported the desorption of both $^{18}\text{O}^-$ and $^{18}\text{OH}^-$ (exp. 3). Performing ESD measurements after further, subsequent exposures to 0.375 ML (exp. 4 and 5) and to 0.625 ML of $^{18}\text{O}_2$ (exp. 6) showed an increase of the integrated yields of $^{18}\text{O}^-$ and $^{18}\text{OH}^-$ at rates dependent on the nature of the SAMs. Following a total exposure equivalent to 1.75 ML of $^{18}\text{O}_2$, each sample was heated to 300 K, and ESD measurements performed every 50 K (exp. 7–11). Under such conditions, a decrease in the integrated yield of $^{18}\text{O}^-$ was seen for SAMs of all types. At 300 K, the integrated yield of $^{18}\text{O}^-$ from all samples was greatly reduced and close to the initial values observed prior to exposure to $^{18}\text{O}_2$.

The production of $^{18}\text{OH}^-$ in Figures 2 and 3 is a significant result, since this moiety cannot be observed unless some chemical reaction has occurred between the added $^{18}\text{O}_2$ (and/or an oxygen fragment) and hydrogen from the SAM. Furthermore, the $^{18}\text{OH}^-$ yield function behavior is clearly related to the amount of $^{18}\text{O}_2$ deposited (Figure 2). In the integrated yield functions of $^{18}\text{OH}^-$ (Figure 3b), warming the samples to 150 K results in an increase of the signal, but only for the SAMs formed from long chain alkanes (i.e., DDT and ODT); the maximum integrated yield is observed at 150 K. For SAMs comprised of short chain molecules (i.e., BT and BM), the behavior of the $^{18}\text{OH}^-$ integrated yield as a function of temperature resembles that for $^{18}\text{O}^-$ integrated yield (Figure 3a). This dependence of the $^{18}\text{OH}^-$ integrated yield on the length of the alkane chains is plausibly related to the resistance towards degradation induced by LEE irradiation for short chains compared to long chains (Figure 1), which was previously observed on alkanethiolate SAMs irradiated by LEEs.^{4,18,19,41} These results suggest that the binding of $^{18}\text{O}_2$ is related to the formation of available sites of attachment in the films during LEE bombardment, thus implying an electron-induced process. The integrated yields of $^{18}\text{O}^-$ and $^{18}\text{OH}^-$ were lower in all experiments for ODT in comparison to DDT. This result is similar as observed in Figure 1, confirming that the emission of H^- by LEE irradiation and the presence of ^{18}O atoms in the SAMs (which is determined by ESD as in Figure 3) are correlated. This result further suggests that the observation of $^{18}\text{O}^-$ and $^{18}\text{OH}^-$ in Figures 2 and 3 is related to an electron-driven process that induces the loss of hydrogen in the SAM. Radicals so formed in the SAM can then be the initial step to bind $^{18}\text{O}_2$ to the film.

The dependence on LEE irradiation for emission of $^{18}\text{O}^-$ and $^{18}\text{OH}^-$ is demonstrated in Figure 4 for the case of DDT, which provides the highest desorption signal. To better understand the origins of these processes, the following procedure was used: (a) SAM films were cooled to 50 K; (b) the films were irradiated for pre-determined periods of time; (c) the samples were exposed to 1.75 ML of $^{18}\text{O}_2$; (d) the samples were heated to 150 K to ensure

that no unreacted $^{18}\text{O}_2$ was still in the films; and (e) the integrated yield functions of $^{18}\text{O}^-$ and $^{18}\text{OH}^-$ were measured by ESD with 2–20 eV LEE range. During the step (b), four “pre-irradiation” periods of time were taken (0, 5, 10 and 20 min) with an incident LEE current of ~ 4 nA, which are equivalent to fluences of 0, 8, 16, and $32 \mu\text{C}/\text{cm}^2$. During this “pre-irradiation” stage, the energy of the LEEs was scanned repeatedly from 0.1 to 18 eV, with an energy step of 0.1 eV, a dwell time of 0.25 s and a sweep time of 45 s. For each “pre-irradiation” period of time, a new sample was used. Absent pre-irradiation, no desorption yields of $^{18}\text{O}^-$ or $^{18}\text{OH}^-$ from SAM films were observed, but both yield functions increased in intensity with the duration of LEE exposure (i.e., electron fluence). This increase is linear until a fluence of $16 \mu\text{C}/\text{cm}^2$ (i.e., 10 min of pre-irradiation), which is consistent with similar experiments on DNA SAMs.²³ Above a pre-irradiation fluence of $16 \mu\text{C}/\text{cm}^2$ some saturation, particularly for $^{18}\text{O}^-$ desorption, is apparent, suggesting that $^{18}\text{O}_2$ molecules are bound to almost all the accessible sites within the SAM or inversely, insufficient $^{18}\text{O}_2$ molecules have been deposited to attach to all the available sites.

Figure 5 shows how the efficiency of attachment of $^{18}\text{O}_2$ to a DDT SAM varies with the energy of LEE pre-irradiation. This dependence was determined using the following procedure. The sample was first cooled to 150 K, i.e., to the temperature which the emission of $^{18}\text{OH}^-$ is optimal (Figure 3). The sample was then irradiated for a period of 10 min (equivalent to a fluence of $16 \mu\text{C}/\text{cm}^2$) at a pre-irradiation energy of 4 eV before being exposed to 1 ML of $^{18}\text{O}_2$. The desorption signals of $^{18}\text{O}^-$ were then measured at $E_i = 6$ eV (i.e., close to the desorption maximum for DEA production of $^{18}\text{O}^-$ in Figure 2). This sequence of procedures was repeated on multiple DDT SAM samples for pre-irradiation energies in the range of 4–20 eV. The ESD $^{18}\text{O}^-$ peak area recorded at 6 eV is plotted against the energy of pre-irradiation in Figure 5a. The intensity of $^{18}\text{O}^-$ desorption is highly dependent on the pre-irradiation energy and a maximum is clearly observed at around 12 eV, suggesting that a resonant process (i.e., formation of a transient negative ion) is involved in the binding of $^{18}\text{O}_2$ to DDT via by electron irradiation. The insert Figure 5b shows in more detail the $^{18}\text{O}^-$ signal in the 6–10 eV region, to better identify the $^{18}\text{O}^-$ emission threshold. In contrast to the data in Figure 5a, these data were recorded using a single DDT SAM sample, which was irradiated and exposed to $^{18}\text{O}_2$, multiple times. The insert shows that, in the case of DDT, a minimum pre-irradiation electron energy of around 7.5 eV is required to observe $^{18}\text{O}^-$ emission. Similar measurements of $^{18}\text{O}^-$ desorption as a function of pre-irradiation energy were performed for BM, BT, and ODT SAMs (Table 1). In each case, a pre-irradiation energy of between 6.5 and 7.5 eV was required to observe $^{18}\text{O}^-$ desorption. A maximum in $^{18}\text{O}^-$ desorption similar to Figure 5a was also observed for each SAM at approximately 12 eV.

4. DISCUSSION

The behaviors observed in the measurements of $^{18}\text{O}^-$ and $^{18}\text{OH}^-$ desorption (for $2 < E_i < 20$ eV) displayed in Figures 2 and 3 imply a reaction between oxygen in the film and surrounding hydrogen to form ^{18}OH complex, as the signal of $^{18}\text{OH}^-$ increases in proportion to the amount of $^{18}\text{O}_2$ deposited. The production of an OH^- desorption signal during electron impact of thin film mixtures of molecular oxygen and various hydrocarbon molecules has previously reported^{42,43} and attributed to *reactive ion scattering*. In this

process, O^- produced by DEA to O_2 initiates hydrogen abstraction by reactions of the type: $O^- + C_xH_{2x+2} \rightarrow (C_xH_{2x+2}O)^{-*} \rightarrow OH^- + C_xH_{2x+1}$. In these earlier works,^{42,43} the production of OH^- was attributed to O^- scattering, rather than H^- interaction with O_2 , because of the similarity between the threshold energies and structure of the O^- and OH^- yield functions, and to gas-phase reports of complex anion formation and reactive scattering.^{44,45} This assignment was also based on the absence of OH^- in gas-phase collisions of H^- with O_2 at low energies.⁴⁶ A somewhat different behavior was in fact observed for O_2 on DNA.²³ The threshold energy for O^- desorption was observed at 3.9 eV, which was 1 eV higher than that of OH^- , suggesting that for that system, OH^- desorption did not derive from reactive scattering of O^- . In the present case, for *n*-alkanethiolate SAMs, the threshold energies for $^{18}O^-$ and $^{18}OH^-$ desorption (Figure 2) are identical, so that reactive scattering by O^- cannot by this measure be discounted as a source of OH^- . However, and similar to the case of O_2 on DNA,²³ it is unlikely that reactive scattering is an important source of OH^- for it is unable to explain the full range of behaviors observed in Figures 2–4.

Indeed, as shown in Figure 4, electron pre-irradiation of the SAMs is necessary to observe desorption of $^{18}O^-$ or $^{18}OH^-$ from SAM films, and desorption depends linearly on the electron fluence, up to an irradiation fluence of $16 \mu C/cm^2$, where a saturation effect appears. The stabilization of $^{18}O_2$ and the persistence of both $^{18}O^-$ and $^{18}OH^-$ signals to elevated temperature similarly requires pre-irradiation and so most probably, involves the binding of O_2 to an alkane damaged site. Effectively, the binding of O_2 to *n*-alkanethiolate films seems to be an electron-induced process which suggests the scission of a C–H bond. This assumption is consistent with earlier results concerning electron irradiated SAMs. Olsen and Rowntree¹⁸ used IR-RAS to monitor the chemical modifications induced by 8 eV electrons in diverse alkanethiolate-based SAMs on Au. They observed that a loss in the intensity of specific bands (CH_2 symmetric/antisymmetric stretch, and CH_3 symmetric stretch) were the main modifications upon irradiation, and concluded that LEEs induce cleavage of C–H bonds principally at sites near the vacuum-film interface. This assumption is also consistent with data from Figure 3a. Effectively, we consider it is unlikely that at 50 K, the $^{18}O_2$ molecules physisorb onto the SAMs, since this temperature is already considerably higher than that usually observed for the sublimation of O_2 under UHV conditions, e.g., 25 K on Pt(111)⁴⁷ or ~33 K on C_{60} .⁴⁸ The decrease in $^{18}O^-$ signal as the sample temperature is raised to 300 K (a process that takes ~60 min), appears too slow to be associated with the evaporation of a physisorbed film, but rather reflects a decrease in the number of sites from which $^{18}O^-$ is desorbed; this suggests that the oxygen atoms that were detected come from $^{18}O_2$ that have become chemically bound to the film.

The integrated yield functions of $^{18}O^-$ and $^{18}OH^-$ in Figure 3 is lower for ODT in comparison to DDT. This trend is also observed for H^- ESD signal in Figure 1. This suggests that the density of the available sites for O_2 bonding is related to the density packing of the SAM. Considering that any decrease of packing in the SAM is associated with a diminution in the density of the C–H bonds, this suggests that the process of formation of O_2 binding sites involves the scission of C–H bonds. The variation of the intensity of $^{18}O^-$ desorption as a function of pre-irradiation electron energy (Figure 5) confirms that the process of oxygen binding is related to such scission. Effectively, the maximum in the $^{18}O^-$ signal, which is associated with a maximum efficiency for binding

oxygen to the SAM, appears at an energy (~12 eV) close to those of i) maxima observed in the ESD of H₂ from various *n*-alkanethiolate SAMs (9–10 eV),^{18,41} and ii) to the ESD yield of H⁻ from *n*-alkanethiolate SAMs in Figure 1 (around 8.5–9 eV). The initial damage process which permits O₂ to bind to the SAM might thus be described as “resonant” and is likely the DEA reaction, $\text{RH} + \text{e}^- \rightarrow (\text{RH})^{*-} \rightarrow \text{R}^\bullet + \text{H}^-$. The apparent difference in the energy of the maxima observed in Figure 5 and in the various ESD experiments may derive from a combination of factors. Firstly, in Figure 5a, we note that the energy step-size in the measurements is 2 eV, and that the pre-irradiation energy at which O₂ is most efficiently attached, is almost closer to 11 eV than 12 eV. Secondly, inspection of Figure 5 suggests that the maximum of the emission is superimposed onto a monotonically increased background. This background may be associated to contributions from direct (i.e., non-resonant) dissociation of the C–H bonds, for example DD or dissociative ionization (i.e., $\text{RH} + \text{e}^- \rightarrow \text{RH}^+ + 2\text{e}^- \rightarrow \text{R}^\bullet + \text{H}^+ + 2\text{e}^-$). Dependent on its energetic threshold, the presence of such a background will cause the position of the maximum in Figure 5 to appear at energies slightly above that of maximum of H⁻ production (Figure 1).

The threshold pre-irradiation energies for attaching O₂ to the various SAMs (as determined by the ESD of ¹⁸O⁻) correlate well with the thresholds for the ESD of H⁻ (Table 1). For each type of SAM studied, the threshold energy for O₂ attachment lies close (i.e., between 0.5 and 1 eV above) that for H⁻ desorption, suggesting a common origin. Here it should be noted that the signal of ¹⁸O⁻ from the irradiated SAMs is at least 2 orders of magnitude less than that of H⁻ from the SAMs, so that for the ¹⁸O⁻ signal, the precision of the present threshold may be limited by the sensitivity of the TOF system. Finally, we note that despite the minor differences in the energies of the maxima of ¹⁸O⁻ emission and for H₂/H⁻ desorption, and between the H⁻ and ¹⁸O⁻ emission thresholds, only DEA has been shown to produce such “resonant” structures at these energies.^{4,18,34,41}

Considering the explanations discussed above for the binding of O₂ onto *n*-alkanethiolate SAMs, the differing behaviors observed in Figure 3 between the integrated yield functions of the various *n*-alkanethiolate SAMs can be understood in terms of the well-known dipole-image dipole quenching model, which is expected to operate when dissociation proceeds via a transient negative ion.^{4,18,19} Since in BT and BM SAMs, the film-vacuum interface (where most electron-induced dissociations occur) is nearer to the metal substrate, quenching of the excited dissociative states increases due to the coupling between the negative charge in the SAM (caused by the presence of the captured incident electron) and the image charge induced in the metallic substrate. The degree of the quenching depends strongly upon the separation between the dipoles since the strength of their coupling is inversely proportional to the third power of this separation.¹⁹ Meanwhile, the lower intensity of ¹⁸O⁻ and ¹⁸OH⁻ for ODT in comparison to DDT is due to the lower packing density of ODT decreasing the density of C–H bonds and thus the available sites for ¹⁸O₂ bonding, as described earlier. At higher energy (above 14 eV), the quenching model cannot fully explain the resistance of short chain alkanes (BT and BM) upon degradation from electron radiation as the dissociation of C–H bonds involves direct processes. This resistance can be a consequence of electronic tunneling from the SAM surface-vacuum interface to the metallic substrate during irradiation. Such an effect has already been observed for different types of SAMs. The electron transfer is usually observed in aromatic-containing SAMs by direct tunneling,

but also in aliphatic-containing SAMs.^{49–51} It has been shown that longer chain length triggers a higher resistance to the charge transfer across the SAM.⁵² Considering that the thickness of the BT SAM is of the order to the BM SAM, the electronic tunneling can explain the resistance upon >14 eV electron irradiation for short chain SAMs. Despite the mechanism of resistance of LEE irradiation, it seems that the binding of O₂ is induced by LEE impact and governed by the length of the molecules of the SAM.

Owing to these observations, we propose that the O₂ binding to SAMs proceed first via dehydrogenation,^{1,18,53} either by the formation of RCH_{x-1}• radicals by DEA or, at higher energies, by randomly-distributed⁴¹ direct processes, occurring preferentially near the surface-vacuum interface.^{4,18,53} These radicals can stabilize (e.g., formation of C=C), react with other degraded alkane molecules to cross-link (i.e., R-CH_{x-1}• + R-CH_{x-1}• → R-(CH_{x-1})-(CH_{x-1})-R),^{1,53} or oxidize in the presence of the deposited oxygen, leading to the formation of peroxy radical (i.e., R(CH_{x-1})OO• and R(CH_{x-1})OOH). The emission of ¹⁸OH⁻ can originate from scission of R(CH_{x-1})OOH groups under LEE irradiation, as the possibility of capture of an hydrogen from the SAM during emission of ¹⁸O⁻ can be neglected because of the decrease of ¹⁸O⁻ with the temperature (Figure 3). Moreover, it has been observed that radiation-induced radicals are produced in thin films and trapped at cryogenic temperatures. Upon heating, combination between radicals can occur like proton transfer across hydrogen bonds.⁵⁴ Considering this observation, the thermally conversion of R(CH_{x-1})OO• into R(CH_{x-1})OOH is more likely the source of the ¹⁸O⁻ decrease and the ¹⁸OH⁻ increase in the ESD signal in Figure 3. As such peroxy groups are not stable in organic materials,⁵⁵ chemical reconfiguration can happen to form more stable species as alcohols, esters, carboxylic acids.

It is also interesting to note that the difference in energy between the DEA-derived maximum in ¹⁸O⁻ desorption (at ~6.7 eV) and that for ¹⁸OH⁻ (~7.7 eV) in Figure 2 is similar to those reported in gas-phase measurements of DEA to several organic acid molecules.^{56,57} The energies of the maxima for both ¹⁸O⁻ and ¹⁸OH⁻ yield functions in Figure 2 are however slightly below to those observed for the gas-phase organic acids. Such an observation is typical of DEA in the condense phase; charge-image induced polarization (*E_{pol}*) lowers the potential energy surface of the dissociative transient negative ion relative to that of the neutral molecular ground state, by about 1 eV, thus reducing the incident electron energy required for DEA.⁵⁸ While the chemical products formed after electron irradiation and O₂ exposure have not been completely identified, the yield function data further supports our hypothesis that the ¹⁸O⁻ and ¹⁸OH⁻ derive from sources such as R(CH_{x-1})OO• and R(CH_{x-1})OOH.

5. CONCLUSIONS

Electron stimulated desorption measurements on various alkanethiols (benzyl mercaptan, 1-butanethiol, 1-dodecanethiol, and 1-octadecanethiol) anchored to a gold substrate, and dosed with ¹⁸O₂, reveal that ¹⁸O⁻ and ¹⁸OH⁻ emission arises from O₂ chemisorption onto the SAM films. The binding of ¹⁸O₂ to SAMs is an electron-induced process, which implies the scission of a C-H bond in the alkane film surface, as the ¹⁸O⁻ and ¹⁸OH⁻ signals increases with electron fluence. Without pre-irradiation of the SAMs, no ¹⁸O⁻ and ¹⁸OH⁻ ESD signals

are observed at elevated temperatures, because $^{18}\text{O}_2$ is unable to bind to the SAMs. A minimum incident electron energy of between 6–7 eV is required to initiate $^{18}\text{O}_2$ binding, which proceed first via the formation of $\text{RCH}_{x-1}^\bullet$ radicals by H^- desorption by DEA or, at higher energies, by the desorption of hydrogen atoms via direct dissociation, and the subsequent formation of the peroxy radical $\text{R}(\text{CH}_{x-1})\text{OO}^\bullet$ and $\text{R}(\text{CH}_{x-1})\text{OOH}$.

These effects were studied as a function of alkanethiol chain length. Lower emission of $^{18}\text{O}^-$ and $^{18}\text{OH}^-$ was seen with short chains, which suggests that the latter are more resistant to degrade upon LEE irradiation. This behavior is likely related to the quenching of the excited dissociative states near of the metallic substrate, or to higher tunneling of higher energy electrons. For long chains, we observe an increase in the ESD yields of $^{18}\text{OH}^-$ and diminution of the $^{18}\text{O}^-$ signals beyond 50 K. Film temperature may cause any un-reacted $^{18}\text{O}_2$ to evaporate or diffuse through the film where they react with $\text{RCH}_{x-1}^\bullet$ sites thus increasing the number of $\text{R}(\text{CH}_{x-1})\text{OOH}$ adducts. Alternatively, and perhaps more plausibly, if the $^{18}\text{O}^-$ signal derives predominantly from reacted $^{18}\text{O}_2$ in the form of $\text{R}(\text{CH}_{x-1})\text{OO}^\bullet$, the increase in $^{18}\text{OH}^-$ signal may correspond to the conversion of $\text{R}(\text{CH}_{x-1})\text{OO}^\bullet$ to $\text{R}(\text{CH}_{x-1})\text{OOH}$. In either case, we see that the anion yields arise from an “Oxygen Fixation” process, similar to that advanced to explain the radio-sensitization properties of O_2 in radiobiology.^{23,27} Thus, the “Oxygen Fixation” mechanism may not be specific to the DNA structure and lead to applications in polymer and surface science.

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Figure 1.
Yield functions of H^- of all pristine SAM samples (0 ML of O_2 at $T = 300$ K).

Figure 2. Yield functions of (a) $^{18}\text{O}^-$ and (b) $^{18}\text{OH}^-$ ESD from a 1-dodecanethiol (DDT) SAM exposed to subsequent doses of $^{18}\text{O}_2$ (0 to 1.75 ML) deposited at a temperature of 50 K.

Figure 3. Variation of energy-integrated (2–20 eV) yield functions of (a) $^{18}\text{O}^-$ and (b) $^{18}\text{OH}^-$ from all SAMs studied under different conditions. The samples were cooled to 50 K, dosed repeatedly with $^{18}\text{O}_2$, and then heated to 300 K.

Figure 4. Variation of integrated yield functions of (a) $^{18}\text{O}^-$ and (b) $^{18}\text{OH}^-$ from DDT SAMs as a function of “pre-irradiation” electron fluence prior exposure to $^{18}\text{O}_2$. The insert graphs are the respective anion yield functions.

Figure 5.

(a) $^{18}\text{O}^-$ peak area from a DDT film as a function of the energy of incident electrons during irradiation of the film prior to its exposure to $^{18}\text{O}_2$. For all energies, the irradiations lasted 10 min (electron fluence of $16 \mu\text{C}/\text{cm}^2$) prior the exposure to 1 ML of $^{18}\text{O}_2$ followed by ESD measurements. (b) The insert shows in more details the yields in the 6–10 eV region, in order to better identify the $^{18}\text{O}^-$ emission threshold.

Table 1

Energetic characteristics of yield function of H^- and $^{18}\text{O}^-$ peak area for all SAMs studied ($E = \pm 0.25$ eV). The temperature at which measurements were made corresponds to that for the maximum of the integrated yield of $^{18}\text{OH}^-$ (Figure 3).

Molecule	H^- Yield Function Threshold (eV)	H^- DEA Maximum (eV)	$^{18}\text{O}^-$ Emission Threshold (eV)	Temperature (K)
Benzyl Mercaptan	5.9	8.4	6.5	50
Butanethiol	6.4	9.3	7.0	50
Dodecanethiol	6.5	8.9	7.5	150
Octadecanethiol	6.4	8.9	7.5	150