

Ozone-Induced Oxidation of Self-Assembled Decanethiol: Contributing Mechanism for “Photooxidation”?

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Several researchers have reported the oxidation of self-assembled alkanethiols on metal surfaces by ultraviolet light (UV) in the presence of air.¹ The photooxidation of alkanethiol self-assembled monolayers (SAMs) is of great interest in a wide range of applications, including photolithography and biotechnology.² However, to date little is known about the mechanism by which these films are photooxidized. In this report, it is demonstrated that ozone can be used to rapidly oxidize alkanethiol SAMs and that the resulting species remaining at the surface have spectroscopic signatures nearly identical to those observed for UV-induced photooxidation. On the basis of similarities in the trends observed for photooxidation and ozone-induced oxidation, coupled with the fact that ozone is generated under typical photooxidation conditions, it is suggested that ozone may have played a role in the observed oxidation of alkanethiol SAMs in past photooxidation studies.

Using secondary ion mass spectrometry and X-ray photoelectron spectroscopy, Tarlov et al. identified a variety of oxidized sulfur species on gold and silver surfaces after UV irradiation of alkanethiol SAMs.¹ In their study, a high-pressure Hg lamp, focused to 3 W/cm², was used for irradiation of samples. Substantial fragmentation of the alkyl chain (60% loss in intensity of the C 1s peak) was observed in addition to the formation of HSO₄⁻, SO₃⁻, and SO₂⁻. Lewis et al. employed surface-enhanced Raman spectroscopy (SERS) to follow the vibrational spectrum of a hexanethiol SAM during irradiation with a low-pressure Hg lamp (3 mW/cm²).³ On the basis of their observations, a mechanism was proposed in which the C–S bond is cleaved by absorption of UV light, the hydrocarbon chain desorbs from the surface, and the remaining sulfur species are rapidly oxidized.

It is well-known that ozone is formed via photolysis of oxygen by light with wavelengths shorter than 242 nm.⁴ Although the principle emission of a low-pressure mercury lamp through a quartz envelope is 254 nm, approximately 3% of the intensity is due to emission at 184 nm.⁵ It is the 184 nm line that generates ozone from air at levels readily detectable by smell, even from the low-intensity (μ W) “Pen-Ray” lamps. For example, a low-pressure Hg lamp with total intensity of 4 mW/cm² produces approximately 1 part per million (ppm) of ozone in a stream of air with a flow rate of 0.5 L/min.⁵ For a 50 W high-pressure Hg lamp, it is estimated that the spectral intensity for wavelengths below 242 nm is ~ 7 mW/cm², which should also result in ppm

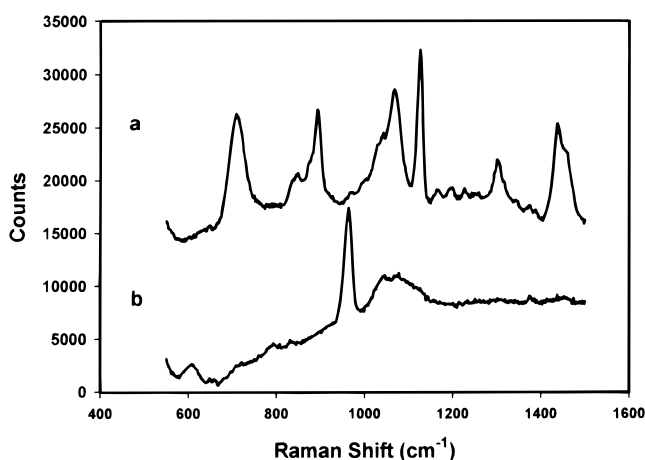


Figure 1. (a) SERS spectrum of decanethiol SAM. (b) SERS spectrum of chemical species remaining on surface after exposure to 16 ppm of ozone (0.22 L/min flow rate). Spectra are not background corrected but have been offset for viewing.

levels of ozone. The local concentration is likely to be higher in the absence of airflow.

In the study reported here, SERS was used to monitor the reaction between ozone and a SAM of decanethiol on a roughened Ag foil;⁶ thus, this study may be *directly* compared with the photooxidation study reported by Lewis et al. for hexanethiol on SERS-active Ag.³ Figure 1a is the SERS spectrum of decanethiol self-assembled onto a Ag foil from a methanol solution.⁷ The spectrum was acquired through a glass sample cell in which the ambient gas was hydrocarbon free air (flow rate 0.22 ± 0.02 L/min). The bands at 1125 and 708 cm⁻¹ are attributed to C–C and C–S stretching modes, respectively.⁸ After acquiring the SERS spectrum of the in-tact SAM, the foil was exposed to a 16 ± 0.1 ppm ozone/air mixture with a relative humidity of $68 \pm 5\%$.⁹ Figure 1b shows the spectrum resulting from chemical species remaining on the Ag surface after 10 min of ozone exposure. The two most prominent bands are at 614 and 963 cm⁻¹. The spectrum in Figure 1b is nearly identical to that published by Lewis et al. after 6 min of exposure to UV light from a low-pressure Hg lamp.³ The two prominent bands in their spectrum, 612 and 958 cm⁻¹, were attributed to adsorbed sulfate ion. Shoulders on the two bands were assigned to adsorbed sulfite ion. On the basis of the comparison of the 10 min exposure spectrum with the Raman spectra of Ag₂SO₄ and Ag₂SO₃ (data not shown), the assignments made by Lewis et al. seem reasonable. It is likely, due to the necessary presence of water for complete reaction to take place, that the adsorbed species are a

(6) The SERS-active substrates were prepared from 1.5 cm \times 1.5 cm, 0.025-mm-thick Ag foils (Aldrich). The foils were cleaned using a sequential four-solvent (hexanes, chloroform, acetone, and methanol) rinse with sonication. The foils were roughened using a previously published procedure (Norrod, K. L.; Sudnik, L.; Rousell, D. J.; Rowlen, K. L. *Appl. Spectrosc.* **1997**, *51*, 994–1001). Self-assembly of decanethiol on the Ag foils was achieved by placing the foils into 0.01 M methanolic solution of decanethiol (99+%, Aldrich) for approximately 24 h.

(7) All spectra shown were acquired using a Detection Limit Raman Microprobe system (DL, Inc.). The system incorporates fiber optic delivery and retrieval of laser light with a high-throughput monochromator (f 2.0). Acquisition times for all spectra were 10 s with a He/Ne laser intensity of approximately 20 mW/cm² at the sample surface.

(8) Bryant, M. A.; Pemberton, J. E. *J. Am. Chem. Soc.* **1991**, *113*, 8284–8293.

(9) Ozone was produced by a custom-built electrical discharge system. For all experiments, hydrocarbon free air (U.S. Welding) was used in the discharge. Ozone was quantified by absorbance at 255 nm through a 5 cm quartz cell (HP 8451A spectrometer). Telfon tubing was used for delivery of gas from the discharge to a glass sample cell. Humidity was measured with a hygrometer (Cole-Parmer).

(1) Huang, J.; Hemminger, J. C. *J. Am. Chem. Soc.* **1993**, *115*, 3342–3343. Huang, J.; Dahlgren, D. A.; Hemminger, J. C. *Langmuir* **1994**, *10*, 626–628. Tarlov, M. J.; Burgess, D. R. F.; Gillen, G. *J. Am. Chem. Soc.* **1993**, *115*, 5305–5306. Tarlov, M. J.; Newman, J. G. *Langmuir* **1992**, *8*, 1398–1405.

(2) For example, see: Kumar, A.; Biebuyck, H. A.; Whitesides, G. M. *Langmuir* **1994**, *10*, 1498–1511. Lercel, M. J.; Rooks, M.; Tiberio, R. C.; Craighead, H. G.; Sheen, C. W.; Parikh, A. N.; Allara, D. L. *J. Vac. Sci. Technol., B* **1995**, *13*, 1139–1143. Li, Y.; Huang, J.; McIver, R. T. J.; Hemminger, J. C. *J. Am. Chem. Soc.* **1992**, *114*, 2428–2432.

(3) Lewis, M.; Tarlov, M.; Carron, K. *J. Am. Chem. Soc.* **1995**, *117*, 9574–9575.

(4) Seinfeld, J. H. *Atmospheric Chemistry and Physics of Air Pollution*; J. Wiley: New York, 1986.

(5) UVP 1996 Catalog (NS-3KL).

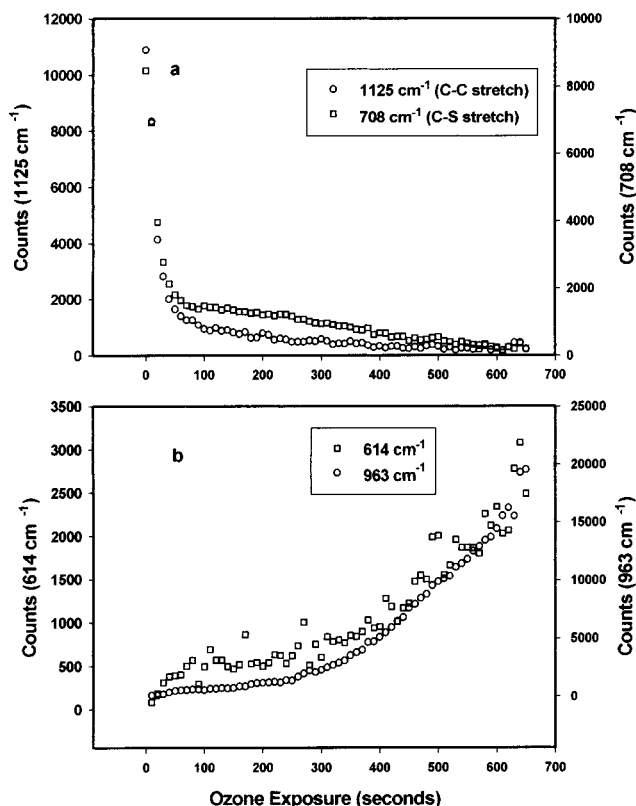


Figure 2. (a, b) Change in specified band intensity as a function of ozone exposure time.

mixture of protonated and nonprotonated ions. It is also possible that the Ag surface is somewhat oxidized; however, the strongest piece of evidence against significant metal oxidation is that a high degree of SERS activity is maintained throughout the experiment, which is not possible on Ag₂O. While further chemical characterization is necessary for unambiguous identification of remaining adsorbed species, the point is that the chemical species produced by ozone-induced oxidation appear to be the same as those produced by photooxidation.

Figure 2a shows the time-dependent loss of C–C and C–S band intensity during exposure to ozone.¹⁰ Growth in band intensity at 614 and 963 cm⁻¹ is shown in Figure 2b. The loss

and subsequent growth of vibrational band intensity, when considered together, exclude the possibility of reorganizational changes in the SAM accounting for spectral differences between exposed and unexposed surfaces. For example, rotation of C–C and C–S bonds from approximately normal to the metal surface, as in a true monolayer, to parallel to the metal surface could result in intensity losses similar to those observed. However, not only is a rotation of ~60° sterically improbable in a monolayer, such a rotation cannot account for intensity growth in the 600–900 cm⁻¹ region. Therefore, loss in band intensity for the C–C and C–S vibrations is taken to be indicative of destruction, or removal, of the hydrocarbon tail. Recall that photooxidation studies also result in a net loss of carbon from the surface.¹ While there appears to be a delay in the growth of the bands associated with SO_x species with respect to the loss of C–C and C–S band intensity, it is difficult to interpret the relative rates. Lewis et al. attributed the delayed onset to the formation of SO_x species only after the alkyl portion of the molecule had been cleaved and desorbed. However, it is also possible that the delay in the growth of these bands is due to low initial concentration of the oxidized species, i.e. the signal is below the detection limit at early times.

Recent work in Paul Bohn's laboratory at the University of Illinois also indicates that ozone, not light, is the species responsible for oxidation of a SAM during "photooxidation."¹¹ The question of oxidation mechanism remains open since the details of ozone reaction at a hydrocarbon/thiol/metal surface are not completely understood. For example, if ozone rapidly degrades on the surface to chemisorbed molecular oxygen and chemisorbed atomic oxygen, which is likely, the true reactive species could be either singlet molecular oxygen or atomic oxygen. To test the influence of molecular singlet state oxygen, Bohn and co-workers co-generated ¹O₂ and O₃ ex situ and observed reaction rates in the presence and absence (removed in stream) of ¹O₂.¹¹ The reaction rate was found to be essentially the same. Clearly, additional studies are necessary to sort out the mechanistic details.

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(10) When air is flowed over the surface at a rate 0.22 L/min, a small (~10%) decrease in the overall SERS spectrum of decanethiol was observed over the period of 30 min. This small change may be due to drying of the SAM (which would change the refractive index of the film).

(11) Zhang, Y.; Terrill, R. H.; Tanzer, T. A.; Bohn, P. W. *J. Am. Chem. Soc.* **1998**, *120*, 2654–2655.