# Reactivity of Sulfur-Containing Molecules on Noble Metal Surfaces. 2. *tert*-Butyl Thioalcohol on Au(110)

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**Abstract:** The adsorption of *tert*-butyl thioalcohol on clean and sulfided Au(110) surfaces has been investigated with temperature programmed reaction spectroscopy. About half of the thiol adsorbed at 100 K undergoes S–H bond cleavage below 300 K to form *tert*-butyl thiolate; $H_2$ and $H_2S$ are evolved between 150 and 350 K, the relative amounts depending on the surface sulfur coverage. *tert*-Butyl thiolate decomposes above 400 K on both clean and sulfided Au(110) surfaces via several competing processes to yield *tert*-butyl thioalcohol, isobutene, and $H_2S$ in the gas phase, together with adsorbed sulfur. The mechanism by which this reaction occurs is dominated by γ-H transfer to either coadsorbed *tert*-butyl thiolate or sulfur–organometallic reactions which may be unique to surfaces.

## 1. Introduction

Our interest in investigating the chemistry of sulfur-containing molecules at Au surfaces is to understand the prospects for the use of gold thin films as sensors for such molecules.[1] Thin gold films undergo measurable resistance changes on exposure to a wide range of sulfur-containing molecules at room temperature, but little is known about the nature of the adsorbed species responsible for the modification of surface properties that causes the resistance change. The adsorption of sulfur-containing molecules on noble metal surfaces is also of interest for comparison with the adsorption of analogous oxygen-containing molecules on the same metals.[2-5] This paper is one of a series elucidating the adsorption and reaction of a number of simple sulfur-containing molecules on clean and sulfided Au(110) surfaces in ultrahigh vacuum (UHV). It discusses in particular the adsorption of *tert*-butyl thioalcohol on clean and sulfided Au(110). We find that the Au(110) surface induces S–H bond cleavage in adsorbed *tert*-butyl thioalcohol and that the thiolate intermediate so formed is stable to above 400 K in UHV. Decomposition leads to the evolution of *tert*-butyl thioalcohol, isobutene, and $H_2S$ into the gas phase. Several competing decomposition routes appear to be involved, including the direct reaction of two thiolate species and reactions of thiolate species with adsorbed sulfur and SH groups. In addition to the work described here and that on $H_2S$,[6] studies will be published on ethanethiol,[7] diethyl sulfide,[7] and benzenethiol.[8]

The reactivity of sulfur-containing molecules at surfaces has been quite extensively studied in the context of the catalysis of hydrodesulfurization reactions of molybdenum systems. Roberts, Friend, and co-workers have elucidated some of the main steps and intermediates in the reactions of thiols and cyclic sulfides on a Mo(110) surface.[9-13] In both cases, the initial step is the

formation of adsorbed thiolate groups. Alkyl thiolates decompose fully to adsorbed sulfur, carbon, and hydrogen on the clean Mo surface, but once the surface is partially deactivated by adsorbed sulfur, alkanes and alkenes evolve from the surface during temperature programmed reaction spectroscopy (TPRS) between 300 and 400 K. The reactions leading to the formation of alkanes or alkenes compete according to the adsorbed hydrogen coverage. In the case of benzenethiol, an adsorbed benzyne intermediate was identified.[10] Benzenethiol adsorption on Ni(110) has also been characterized; benzene and hydrogen are the only gas-phase products.[14]

Methanethiol adsorption has also been rather widely studied, mainly by the techniques of TPRS and electron energy loss spectroscopy (EELS). On Pt(111),[15,16] Ni(110),[17] Ni(100),[18] Ni(111),[19] Fe(100),[20] Mo(110),[21] and W(211),[22] complete decomposition of adsorbed methanethiol is observed, together with the formation of methane at higher exposures. Discussion of the mechanism for methane formation centers on the degree to which C–S bond cleavage precedes hydrogen addition. On Cu(100),[23] the chemistry of methanethiol, dimethyl sulfide, and dimethyl disulfide has been briefly compared. Dimethyl sulfide adsorbs purely molecularly, while methyl thiolate was formed from the other two species. Decomposition of methyl thiolate yielded methane, ethane, and dihydrogen as gas-phase products in TPRS together with adsorbed sulfur. Structural studies have been made of methyl thiolate on several surfaces.[15,24,25] Both linear and bent metal–S–C geometries have been identified, depending

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possibly on the route of formation. Electrochemical studies have also been made of thiol adsorption on Ag(111) and Pt(111),[26] and the thiolate species so formed characterized via EELS, AES, and LEED. Exclusively linear metal–S–C geometries were found. This method of formation of the adsorbed layers differs from those discussed earlier in that the thiolate layer is formed under equilibrium conditions and electric fields are present that may alter its orientation.

A recent surface enhanced Raman spectroscopy (SERS) study of the adsorption of benzenethiol, diphenyl sulfide, and diphenyl disulfide on gold films reported thiolate formation in all three cases.[27] Contrasting results have been obtained for methanethiol and dimethyl disulfide adsorption on Au(111) in UHV.[28] Methanethiol was found to adsorb purely molecularly, while in the case of dimethyl disulfide, methyl thiolate formation and subsequent recombination with no decomposition was reported. This final study was performed in the context of the characterization of self-assembled monolayers of long-chain alkyl thiolates on gold thin films by adsorption from solvent. In these cases, the character of the film is to a large extent controlled by the many interactions between the hydrocarbon chains.[29,30] A recent scanning tunneling microscopy (STM) study compared ethyl thiolate and octyl thiolate adsorption from solution onto Au-(111).[31] In the case of ethyl thiolate, a highly ordered film was formed, characterized by close packing of thiolate groups in a ($\sqrt{3} \times \sqrt{3}$)R30° structure. LEED has also been used to make structural comparisons between adsorbed thiolate layers formed from $C_1$ through $C_{22}$ thiols on Au(111) and Au(100) surfaces.[32]

It is only relatively recently that the *chemistry* as opposed to the structure of organometallic systems containing thiol, thiolate, and sulfide ligands has been studied in any detail.[33-37] In general, the problem has been the *ease* with which S–H and C–S bond cleavages occur. Nickel-based systems have been of particular interest from the point of view of synthetic processes based on rather selective C–S bond cleavage, and mechanisms based on radical reactions, hydrogen transfer, and electron transfer have all been proposed. No studies on the reactivity of gold–thiolate systems seem to have been performed.

## 2. Experimental Techniques

The experiments reported here were performed in a stainless steel ion-pumped ultrahigh vacuum chamber with a base pressure of $8 \times 10^{-11}$ Torr. The chamber was equipped with a 0.5-in. diameter tube doser and a UTI 100C quadrupole mass spectrometer (QMS) interfaced to an IBM microcomputer for the acquisition of multiplexed temperature programmed desorption (TPRS) data. The mass spectrometer ionizer was collimated by a glass cap. Surface characterization via AES, XPS, and LEEd was also available. The Au(110) crystal could be cooled to 95 K via a liquid nitrogen reservoir and radiatively heated to above 700 K. The surface was cleaned by cycles of Ar$^+$ ion bombardment (400 V, 13 $\mu$A) and anneals at 700 K. In this way, surfaces were generated free from the major contaminants Si, S, C, and Ca (limit of sensitivity was 2%). Surfaces were dosed at 95 K by placing the crystal about 5 mm in front of the doser (a distance approximately equal to the diameter of the crystal). The crystal was then rotated to the QMS, positioned about 5 mm from the 3-mm-diameter hole in the QMS collimator, and heated at a typical

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(38) Sulfur coverage determined from results on $H_2S$ adsorption on Au-(110).[6]
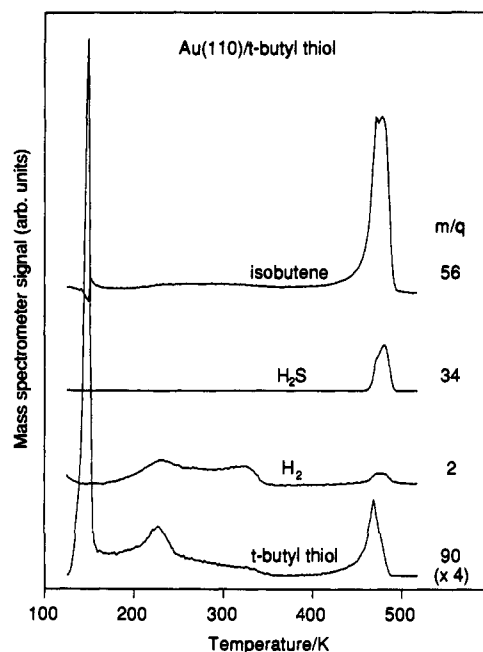
**Figure 1.** Temperature programmed reaction spectra for a multilayer coverage of *tert*-butyl thioalcohol adsorbed onto clean Au(110) at 95 K. The traces shown have been corrected for the cracking of higher molecular weight species (see text).

rate of 10 K s$^{-1}$. The temperature was measured using a chromel–alumel thermocouple pressed tightly against the Au(110) crystal. TPRS experiments were performed with the crystal biased at –90 V relative to ground to prevent electron beam induced decomposition of adsorbates,[6] particularly from the mass spectrometer ionization filament, which was operated at 55 V below ground potential. The use of an isolation amplifier enabled thermocouple readings to be recorded on the computer in these circumstances. *tert*-Butyl thioalcohol (99% purity, Aldrich) was purified daily before use by several freeze–pump–thaw cycles, and the stainless steel dosing lines were passivated toward decomposition by repeated exposure to this and other sulfur-containing molecules.

## 3. Results

A temperature programmed reaction spectrum for *tert*-butyl thioalcohol adsorbed onto a clean Au(110) surface at 100 K is shown in Figure 1. Traces are shown for $m/q$ values of 2, 34, 56, and 90. Corresponding data for adsorption onto a partially sulfided Au(110) surface, obtained by the prior exposure of the Au(110) surface to five *tert*-butyl thioalcohol doses similar to that in Figure 1 ($\theta_S = 0.15^{38}$), are shown in Figure 2. All the traces for $m/q$ less than 90 have been corrected for cracking of *tert*-butyl thioalcohol by the subtraction of the appropriate fraction of the $m/q = 90$ spectrum (molecular ion of *tert*-butyl thioalcohol). The fraction to be subtracted was that needed to null out the sharp low-temperature multilayer *tert*-butyl thioalcohol desorption feature which appeared in all the uncorrected spectra at 160 K. The relative fractions thus derived constitute a cracking spectrum for *tert*-butyl thioalcohol which is consistent with published spectra,[39,40] except for the observation of excess amounts for $m/q$ values of 56, 39, 41, 40, and 55. All these masses correspond to cracking fragments of isobutene. Since the amounts of these fragments relative to $m/q = 90$ are constant and independent of the state of the surface and since no sulfur is deposited on the surface in this temperature regime (see later), these fragments are attributed to the chemical cracking of *tert*-butyl thioalcohol on hot surfaces inside the can around the mass spectrometer ionizer to form isobutene, which is itself subsequently ionized and detected. Similarly, small amounts (apparent coverage) of 34

(39) Cornu, A.; Massot, R. *Compilation of Mass Spectral Data*; Heyden and Sons Ltd.: London, 1966; 1st suppl., 1967, 2nd suppl., 1971.

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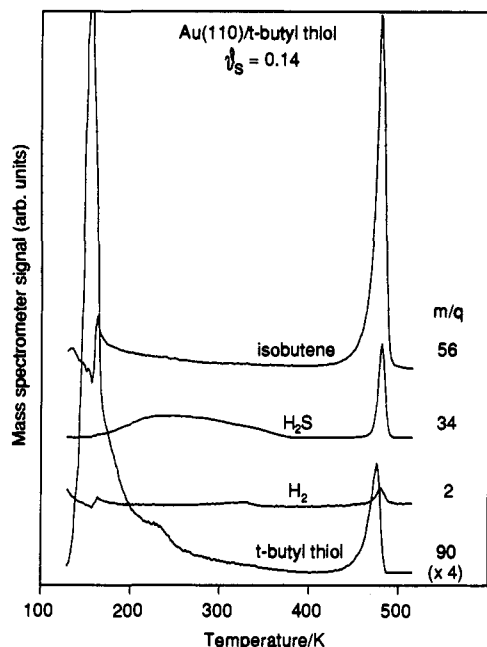
(41) See also discussion in ref 2.

**Figure 2.** Temperature programmed reaction spectra for a multilayer coverage of *tert*-butyl thioalcohol adsorbed onto a partially sulfided Au-(110) surface at 95 K. On adsorption $\theta_S = 0.14$, generated by five previous exposures to *tert*-butyl thioalcohol.

(H$_2$S) that are observed coincidentally with *tert*-butyl thioalcohol are attributed to reaction in the mass spectrometer also. The cracking fractions determined above are also used to correct the high-temperature desorption peaks, on the assumption that the same ratios are appropriate.[41] Over the temperature range 160–340 K for molecular desorption of *tert*-butyl thioalcohol, the cracking fractions *are* constant, since all the fragments show the same peak shape as $m/q = 90$.

On both the initially clean and partially sulfided surfaces, desorption from a multilayer of *tert*-butyl thioalcohol occurs around 160 K, followed by desorption from chemisorbed states up to about 340 K. In the presence of sulfur, a new chemisorption state is seen at about 180 K. The desorption peak temperature for the multilayer corresponds to an activation energy of 39.6 kJ mol$^{-1}$.[42,43] Desorption from chemisorbed states is accompanied by the desorption of hydrogen (Figures 1 and 2) and/or hydrogen sulfide (Figure 2). No H$_2$S is evolved below 400 K when the Au(110) surface is initially free of sulfur. As the sulfur coverage progressively increases with successive exposures (monitored via AES between each exposure experiment), the amount of H$_2$S desorbing in this temperature range increases while the amount of H$_2$ decreases. The H$_2$ evolution occurs at two peaks of roughly equal intensity at 230 and 330 K on the surface free of sulfur, and at 330 K alone on the partially sulfided surface. H$_2$S desorption shows a broad peak at 210–240 K, with a tail stretching to 375 K.

Above 400 K several different species are evolved with nearly coincident peak temperatures (Figure 3). *tert*-Butyl thioalcohol was clearly identified at about 470 K. In other experiments all masses between 34 and 190 were monitored, and no fragments above 90 were observed. Experiments with benzenethiol indicated that the instrument is capable of detecting masses up to at least $m/q = 186$ with high sensitivity.[8] The other main species desorbing was identified as a butene. On the basis of the main cracking fragments observed, isobutene cannot be distinguished from other butenes, but it is obviously the most chemically



**Figure 3.** Temperature programmed reaction spectra above 400 K to show product evolution from *tert*-butyl thiolate decomposition on clean and sulfided Au(110) surfaces. As Figures 1 and 2. $\theta_S = 0.06$ at onset of decomposition on the sulfided surface.

plausible product. H$_2$S desorbs at 470–480 K, and a small amount of H$_2$ desorbs at 480 K, together with a small amount of butane (estimated as only about 0.5% of total evolved organics[44]). After heating a surface covered with *tert*-butyl thioalcohol to 600 K, only sulfur is left behind on the surface; no carbon is deposited to the sensitivity limit in AES. On an initially clean Au(110) surface, the coverage of sulfur deposited is 0.08, and with repeated dosing, the sulfur coverage increases to 0.15.

## 4. Discussion

**4.1. Reactions Occurring below 400 K.** We attribute the desorption of hydrogen and hydrogen sulfide below 350 K to the activation of adsorbed *tert*-butyl thioalcohol by either the clean or sulfur-modified Au(110) surface, to form an adsorbed thiolate intermediate which subsequently decomposes above 400 K to yield *tert*-butyl thioalcohol and isobutene. We identify that intermediate as *t*-butyl thiolate, as explained below.

The evolution of H$_2$ from *tert*-butyl thioalcohol adsorbed on a clean Au(110) surface indicates that the Au(110) surface itself induces S–H bond cleavage in adsorbed *tert*-butyl thioalcohol. This contrasts with the low activity of the same surface for S–H bond activation in H$_2$S,[6] but it is consistent with the significantly weaker S–H bond strength in thiols compared to H$_2$S (369 versus 387 kJ mol$^{-1}$).[45] On the initially clean surface, more than one H$_2$ desorption peak is observed. The peak at 230 K is only slightly higher in temperature than that observed for H atom recombination on the clean Au(110) surface,[46] and on the sulfided surface,[47] and is therefore attributed to the desorption-limited recombination process of H atoms, modified by the presence of coadsorbed species. Therefore, some S–H bond cleavage clearly occurs below this temperature. Further reaction of adsorbed thiol also occurs at higher temperatures, as indicated by the reaction-limited evolution of H$_2$ up to 350 K. The observation of a second H$_2$ desorption peak may indicate that a second reaction channel with

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(43) Though this is a zero-order process, we can estimate the activation energy by using Redhead's equation for a first-order process and assuming a preexponential factor of $10^{13}$ s$^{-1}$.
(44) This figure is based on the quantification scheme described later, and on published cracking fractions,[39,40] estimated ionization probabilities,[2] and spectrometer characteristics for butane *relative* to butene.
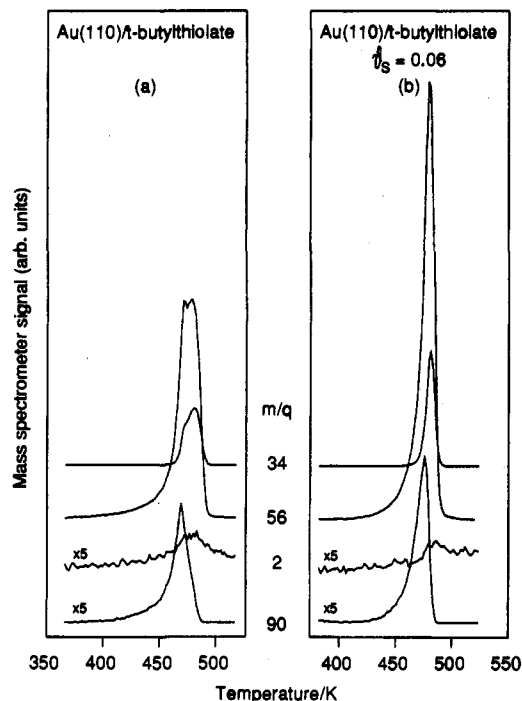
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a higher activation energy is opened at higher temperature, or it may merely reflect the freeing of available sites for the cleavage reaction through *tert*-butyl thioalcohol desorption.

On the partially sulfided surface, $H_2S$ desorbs over a wide temperature range from 150 to 375 K. Molecularly adsorbed $H_2S$ has been found to desorb over the range 150–250 K from Au(110).[6] Above this temperature the generation of adsorbed $H_2S$ must be rate-limiting. $H_2S$ formation may occur either through the direct attack of adsorbed sulfur or adsorbed SH groups on the thiol group or by the reaction of sulfur and SH with adsorbed hydrogen, formed by the activation of the S–H bond of the thiol by the Au(110) surface itself. The direct attack of sulfur on the thiol group is analogous to the behavior observed in the coadsorbed sulfur/hydrogen sulfide system, that is, the reaction of S and $H_2S$ to form 2SH. In experiments involving electron beam induced decomposition of adsorbed $H_2S$ on Au-(110), it was found that H + H recombination was much faster than a possible sequence of S + H recombination steps to form $H_2S$.[48] Hence, the $H_2S$ observed here must involve the direct reaction of S or SH with adsorbed thiol, since little or no $H_2$ evolution occurred from this surface.

It is clear that, when *tert*-butyl thioalcohol is adsorbed on a sulfided surface, $H_2S$ desorbs below 400 K. Since *no* $H_2S$ is evolved from the initially clean surface in the low-temperature region, and since adsorbed $H_2S$ readily desorbs below 400 K,[6] we can conclude that no free sulfur is generated on this surface below 400 K, that is, no C–S bond cleavage occurs in this temperature range.

Since all decomposition of the adsorbed species occurs over a very narrow temperature range near 480 K on both the clean and sulfur-modified surfaces, it is likely that only a single intermediate is formed. C–H bond cleavage, S–H bond cleavage, and C–S bond cleavage are the three possible processes involved in forming the intermediate. C–H bond cleavage at an unactivated carbon center is not anticipated on a gold surface in this temperature range (see section 4.5 below).[2-5] The formation of alkyl groups via C–S bond cleavage can be ruled out for several reasons: firstly, no free sulfur or SH is generated below 350 K since no $H_2S$ desorbs in this temperature range for the first exposure on the clean surface; secondly, alkyl groups generated by photon induced decomposition of alkyl halides desorb recombinatively below 200 K from the chemically similar Ag(111) surface,[49] and no recombination products are seen here; thirdly, the decomposition of alkyl groups would not readily lead to the evolution of *tert*-butyl thioalcohol. Thus *tert*-butyl thiolate groups formed through S–H bond cleavage are the most likely product of *tert*-butyl thioalcohol adsorption on either the clean or sulfided Au(110) surface. Further evidence comes from studies performed with isotopically labeled ethanethiol, $C_2H_5SD$.[6] Significantly less conversion to thiolate was observed for $C_2H_5SD$ adsorbed on Au(110) than for $C_2H_5SH$, as expected for a normal kinetic isotope effect in S–H/D bond cleavage. In addition, none of the high-temperature decomposition products contained deuterium, again indicating that the S–H/D bond was cleaved in formation of the intermediate.

**4.2. Decomposition of *tert*-Butyl Thiolate above 400 K.** It is clear from the complex peak shapes in the TPRS traces for the 480 K decomposition process that more than one reaction pathway must be operating (Figure 3). Initially the *tert*-butyl thioalcohol trace rises with a peak shape identical to that of the isobutene trace (Figure 4), but subsequently it falls with the onset of $H_2S$ desorption. No $H_2S$ or $H_2$ desorption accompanies the leading edge of *tert*-butyl thioalcohol and isobutene desorption. It is relevant to note that the correction applied to the isobutene

(48) When a Au(110)/$H_2S$ surface was exposed to electrons and heated $H_2$ desorbed at 215 K and $H_2S$ at 300 K.[6] Since molecular $H_2S$ desorbs below 250 K, the 300 K state is attributed to an SH disproportionation reaction. The fact that no $H_2S$ desorbs from molecular states indicates that the H + H reaction is faster than either the S + H reaction or the SH + H reaction or both.

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**Figure 4.** Desorption traces for *tert*-butyl thioalcohol and isobutene for *tert*-butyl thiolate decomposition on clean Au(110); the trace for *tert*-butyl thioalcohol has been scaled by a factor of 5.7 to show the identical leading edges.

spectrum to account for the cracking of *tert*-butyl thioalcohol was a subtraction of $(0.7 \times$ thiol intensity at $m/q = 90)$. Here the isobutene signal intensity at $m/q = 56$ that accompanies *tert*-butyl thioalcohol desorption is about a factor of 6 larger than the *tert*-butyl thioalcohol intensity at $m/q = 90$. Thus the observed isobutene intensity after correction cannot be attributed to more cracking of *tert*-butyl thioalcohol in the spectrometer. Instead *tert*-butyl thioalcohol and isobutene are desorbing coincidentally in the leading edge. Note that the peak shapes shown in Figures 1–3 *are not artifacts of the subtraction process*; they appear with equal clarity in the raw data.

It is useful to consider the stoichiometry of the decomposition of *t*-butyl thiolate, bearing in mind that no carbon is deposited and that the only products observed are *tert*-butyl thioalcohol, isobutene, hydrogen sulfide, hydrogen, and adsorbed sulfur, together with a small amount of butane. Overall reaction channels that are consistent with these observations are as follows:

$$2C_4H_9S \rightarrow C_4H_9SH + C_4H_8 + S$$

$$2C_4H_9S \rightarrow 2C_4H_8 + S + H_2S$$

$$2C_4H_9S \rightarrow 2C_4H_8 + 2S + H_2$$

$$2C_4H_9S \rightarrow C_4H_8 + C_4H_{10} + 2S$$
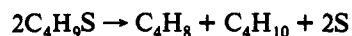
The last of these reaction processes is not significant since we estimate that only about 0.001 monolayers (ML) of butane desorbs,[44] relative to a total thiolate coverage of about 0.18 ML (see next section). Note that the first two of these reactions lead to the deposition of one sulfur atom for every two thiolate groups reacting, while the last two reactions deposit one sulfur atom for each thiolate species. Since each sulfur atom on the surface can react with a thiol at low temperature to form two thiolate species, it is only the presence and extent of the reactions that generate $H_2$ at high or low temperature that lead to the buildup of sulfur on the surface. We can determine the sulfur coverage at any point by measuring the amount of $H_2S$ and other products that have desorbed, using the quantification scheme described below. The gross branching ratios between the different reaction channels are apparently relatively independent of the sulfur coverage on the surface, as

**Figure 5.** Amount of *tert*-butyl thiolate formed from *tert*-butyl thioalcohol adsorption and amounts of *tert*-butyl thioalcohol, H$_2$S, isobutene, and H$_2$ generated above 400 K from *tert*-butyl thiolate decomposition as a function of surface sulfur coverage on adsorption. Amounts quoted as fractions of a monolayer (1 ML = 8.54 × 10$^{14}$ molecules cm$^{-2}$).

indicated by the relative amounts of isobutene and *tert*-butyl thioalcohol that desorb. About two-thirds of the adsorbed thiolate yields *tert*-butyl thioalcohol and isobutene, and about one-third yields isobutene and H$_2$S or H$_2$, independent of surface sulfur coverage over the range studied ($\theta_S = 0$ to $\theta_S = 0.08$ at the initiation of decomposition).

**4.3. Quantification of *tert*-Butyl Thiolate Coverage and Product Yields.** In earlier work we determined the monolayer coverage of H$_2$S on Au(110) to be 0.77 ± 0.04.[6] Using the mass spectrometer sensitivity factor for H$_2$S obtained through that calibration, we were able to quantify the absolute coverages of H$_2$S desorbing from the surface in the experiments performed here. Using the data from a number of different experiments, we were then able to determine mass spectrometer sensitivity factors for the other species which desorb form the surface, namely H$_2$, *tert*-butyl thioalcohol, and isobutene, and hence quantify the absolute coverages of *tert*-butyl thiolate generated and the amounts of the various different products. The details of the analysis are given in the Appendix. The relative amounts so calculated of the different products generated during a series of experiments with increasing surface sulfur coverages are shown in Figure 5.

The thiolate coverage generated for *tert*-butyl thioalcohol adsorption onto clean and sulfided Au(110) rises from about 0.15 on the clean Au(110) surface to about 0.18 on a surface with a sulfur precoverage of 0.15. The presence of sulfur on the surface can affect the amount of thiolate formed in two ways: firstly, it can increase the amount of thiolate formed by providing an alternative pathway for its formation, and secondly, adsorbed sulfur can also *inhibit* thiolate formation by preventing thiol molecules from contacting the Au surface.[50] The maximum coverage of *tert*-butyl thiolate that is formed is much less than that possible on the basis of close packing of adsorbed thiol or

thiolate species, expected to be about 0.3–0.4[51] for the thiol on the basis of close packing of molecules with van der Waals dimensions,[52,53] while for *tert*-butyl thiolate, the maximum coverage possible is 0.4–0.5. The *thiol monolayer coverage adsorbed at 100 K* varies between about 0.31 and 0.39, as estimated from the sum of the amount of thiol which desorbs between about 150–160 and 350 K and the amount of thiolate which subsequently decomposes to thiol and isobutene above 400 K, in reasonable agreement with the maximum thiol/thiolate coverages estimated above. Since the sulfur coverage varies from 0 to about 0.15, it appears that sulfur does not block thiol adsorption or thiolate formation in this coverage range.

In experiments involving adsorption from solution, the densities of thiolate formed approach the close packed densities.[30–32] The reason why such thiolate densities are not achieved here is that the conversion of thiol to thiolate is competitive with thiol desorption, and in UHV, desorption of thiol is an irreversible process. In solution, however, continual desorption and readsorption of thiol are possible under the conditions when S–H scission is occurring. One other difference between the two systems, which may limit the thiolate coverage obtained in UHV, lies in the fate of the sulfhydryl hydrogen. In the single crystal UHV system, it either desorbs as dihydrogen or is abstracted by adsorbed sulfur to form SH and H$_2$S. Adsorbed H, SH, and H$_2$S may all compete for sites with the thiolate and thiol; the fixed number of these sites may limit the reaction until some of the adsorbed thiol or product has desorbed. The fate of hydrogen in the solution-based thiol to thiolate conversion has not been characterized, and it may cause less interference.

**4.4. Possible Pathways for the Decomposition of *tert*-Butyl Thiolate.** There are a number of mechanisms that can be envisaged for the decomposition of *tert*-butyl thiolate on Au-(110) to give the observed thiol, isobutene, and H$_2$S. These mechanisms involve hydrogen transfer from the thiolate either to the Au(110) surface, or to adsorbed sulfur, or to another adsorbed thiolate group directly. *tert*-Butyl thiolate decomposition on the clean Au(110) surface (Figure 1) cannot *initially* involve sulfur as a reactant in the decomposition process; the absence of H$_2$S desorption on the initially clean surface means that there can be no adsorbed sulfur present. Decomposition could occur via a disproportionation reaction between two thiolate species; we can envisage the attack of the thiolate sulfur on the $\gamma$-H[54] of another thiolate species to yield a thiol molecule together with isobutene and adsorbed sulfur:

$$2C_4H_9S_{(a)} \rightarrow C_4H_9SH_{(g)} + C_4H_{8(g)} + S_{(a)} \qquad (1)$$

At the opposite limit, the products can be formed in a stepwise fashion, generating adsorbed hydrogen and adsorbed alkyl groups or possibly metallocycle species depending on whether C–S bond cleavage precedes C–H bond cleavage:



$$C_4H_9S_{(a)} \longrightarrow C_4H_{9(a)} + S_{(a)} \qquad (2a)$$

$$(2b,c)$$

$$+ H_{(a)} \longrightarrow C_4H_{8(g)} + S_{(a)} + H_{(a)} \qquad (2d)$$

$$C_4H_9S_{(a)} + H_{(a)} \longrightarrow C_4H_9SH_{(g)} \qquad (2e)$$

For several reasons we conclude that the generation of *tert*-butyl thioalcohol and isobutene *in this temperature regime* occurs via a process like reaction 1. It is observed experimentally that on the clean surface *tert*-butyl thioalcohol and isobutene desorb with identical peak shapes (Figure 4), and in equal amounts,

(50) The initial thiol coverage adsorbed may also play a role. In all cases the surfaces were initially covered with more than a monolayer of *tert*-butyl thioalcohol, though the amount adsorbed was not constant, and increased throughout the series of experiments, due either to a sulfur-dependent sticking coefficient or to changes in doser characteristics with time. Since formation of the thiolate competes with desorption of the thiol, the amount of thiolate formed will vary slightly with experiment due to slight changes in heating rate.

(51) Coverage is defined with respect to the Au(110) surface atom density of 8.54 × 10$^{14}$ cm$^{-2}$.

(52) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

(53) The uncertainty in coverage comes from whether the molecules adopt upright or tipped conformations.

(54) The $\gamma$-C–H bond is so labeled with respect to the metal center.
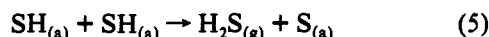
along the leading edge for decomposition, with negligible formation of $H_2$, $H_2S$, butane, or 2,2,3,3-tetramethylbutane. Once decomposition has proceeded to some degree, however, $H_2S$ and a small amount of $H_2$ are evolved. Neither the $H_2S$ nor the $H_2$ signals track the leading edges of the isobutene and *tert*-butyl thioalcohol peaks. Now, $H_2$ recombinative desorption occurs on both the clean and sulfided Au(110) surface at about 215 K, and alkyl groups formed by the photoinduced decomposition of alkyl halides have been found to desorb recombinatively below 200 K from the chemically similar Ag(111) surface. Therefore, the evolution of $H_2$ and 2,2,3,3-tetramethylbutane, together with the formation of isobutane, ought to be observed if the formation of adsorbed hydrogen atoms or *tert*-butyl groups is the dominant decomposition route.[55] Further evidence that thiolate decomposition does not involve the formation of adsorbed hydrogen atoms is the fact that at 350 K during TPRS adsorbed *tert*-butyl thioalcohol *decomposes* to form the thiolate and adsorbed hydrogen atoms, which desorb as dihydrogen in preference to recombining with the thiolate.[56] It is unlikely that the reaction selectivity could change so markedly between 350 and 450 K that reaction 2e would totally consume adsorbed hydrogen atoms, as is required by the experimental observations. The bulk of the evidence does support the hydrogen transfer process of equation 1.

As the temperature and/or the surface sulfur coverage increases during TPRS, $H_2S$ evolution begins. $H_2S$ formation could, in principle, occur via successive recombination of adsorbed sulfur and hydrogen atoms. However, over the temperature range from 150 to 350 K, it is clear that H + H recombination is much faster than H + S and/or H + SH recombination processes,[57] and it is therefore unlikely that $H_2S$ formation via recombination would become quite as dominant above 450 K as is required to give the observed product distribution.

The alternative mechanism for forming $H_2S$ is the extraction of $\gamma$-H from a thiolate species by adsorbed sulfur to form adsorbed SH and isobutene and sulfur:

$$C_4H_{9}S_{(a)} + S_{(a)} \rightarrow C_4H_{8(g)} + SH_{(a)} + S_{(a)} \qquad (3)$$
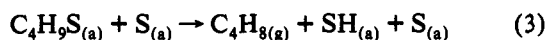
Adsorbed SH can itself react with thiolate to form isobutene and $H_2S$ (eq 4), or it can react with another SH species to form $H_2S$ and adsorbed sulfur (eq 5):

$$C_4H_{9}S_{(a)} + SH_{(a)} \rightarrow C_4H_{8(g)} + H_2S_{(g)} \qquad (4)$$

$$SH_{(a)} + SH_{(a)} \rightarrow H_2S_{(g)} + S_{(a)} \qquad (5)$$

However, reactions 4 and 5 are not the only reactions available to adsorbed SH. SH can also react with adsorbed thiolate in a reaction chemically analogous to reaction 5, forming thiol and adsorbed sulfur. Reaction 5 has previously been observed on Au(110).[6]

$$C_4H_{9}S_{(a)} + SH_{(a)} \rightarrow C_4H_9SH_{(g)} + S_{(a)} \qquad (6)$$

Reactions 1, 3, and 4 are all chemically analogous and involve the abstraction by sulfur of a hydrogen atom bound to carbon.

The mechanism we have described is essentially an elimination reaction involving S–Au as the leaving group, and adsorbed sulfur,



**Figure 6.** Plot of ln(desorption yield/(thiolate coverage)$^2$) versus the reciprocal temperature for *tert*-butyl thiolate decomposition above 400 K on initially clean Au(110) and on sulfided Au(110) ($\theta_S$ = 0.06).

sulfhydryl, or thiolate as the base. The issue requiring justification is the proposed abstraction of hydrogen from an *unactivated* carbon center. Activated C–H bonds are those that lie $\alpha$ to a heteroatom or to an unsaturated center, and the energy required to remove the proton is reduced because the transition state is stabilized by the neighboring heteroatom or unsaturated center. The abstraction of hydrogen bound at an *activated* carbon center by adsorbed oxygen has been proposed frequently to explain the reactivity of molecules on silver and gold surfaces.[2–5]

The mechanism of the formation of alkenes from alkyl thiolates adsorbed on Mo(110) has also been attributed to abstraction of an unactivated $\gamma$-H atom.[9–12] In the case of *tert*-butyl thiolate, a radical transition state for $\gamma$-H abstraction involving substantial breaking of the C–S bond was proposed to explain the preference for $\gamma$- over $\beta$-H abstraction,[13,58] since weakening of the C–S bond will reduce stabilization of the transition state for $\beta$-H abstraction. Access to a similar transition state at 600 K on Au(110) is reasonable. We propose that in the Au(110) system, however, hydrogen transfer occurs not to the metal but to adsorbed sulfur species—sulfur atoms, SH groups, or thiolate groups. This explanation also agrees with the observed correlation of the temperature corresponding to the maximum rate of decomposition and the relative C–S bond strengths of *tert*-butyl thioalcohol ethanethiol, and benzenethiol (*t*-BuSH, 475 K and 284 kJ mol$^{-1}$; EtSH, 525–550 K and 296.6 kJ mol$^{-1}$; PhSH, 600–630 K and 356.4 kJ mol$^{-1}$). In the case of methyl thiolate decomposition on other metals, authors have varied in their opinion as to whether C–S bond cleavage precedes or is accompanied by hydrogenation.

The mechanistic description of thiolate decomposition presented above is also consistent with other details of the experimental observations. The activation energy for *tert*-butyl thioalcohol and isobutene formation was estimated by assuming a reaction second order in thiolate coverage (Figure 6).[59,60] A value of 80 kJ mol$^{-1}$ was obtained from the slope of the leading edge for *tert*-butyl thioalcohol evolution from the surface initially clean of sulfur, while on the partially sulfided surfaces, a similar plot yields a value of 160 kJ mol$^{-1}$ ($\theta_S$ = 0.06 at the onset of

(55) Hydrogen atom recombination does, however, show an unusually low preexponential factor and activation energy on gold surfaces, with the consequence that the probability of hydrogen atom recombination rises rather slowly with increasing temperature: Bruce Kay, Batelle Northwest, private communication.

(56) Recombination of adsorbed hydrogen and the thiolate to form the thiol is excluded on the basis that the peak shapes for $H_2$ and thiol evolution are the same.

(57) When a surface with adsorbed $H_2S$ is exposed to electrons and subsequently heated, $H_2$ desorbs at about 215 K and $H_2S$ desorbs at 300 K via SH disproportionation; no $H_2S$ desorbs from the molecular adsorption states up to 250 K. When S–H bond cleavage occurs in adsorbed thiol during a TPRS flash, $H_2$ desorbs recominatively even though sulfur is present on the surface.
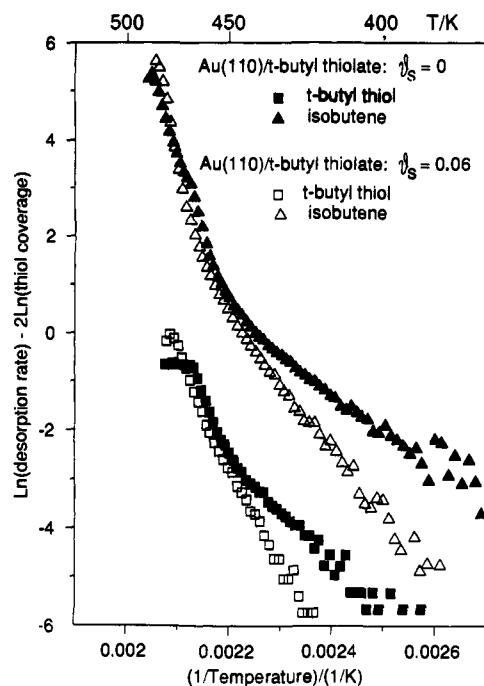
(58) Wiegand, B. C.; Friend, C. M. *Chem. Rev.*, in press.

(59) Falconer, J. L.; Madix, R. J. *J. Catal.* 1977, *48*, 262.

(60) The thiolate coverage was calculated using mass spectrometer sensitivity factors determined by the quantification model discussed in the Appendix.

decomposition),[61] indicating a stabilization of the adsorbed thiolate by adsorbed sulfur.[62,63] In Figure 6, the slope of the plot for the surface initially free or sulfur remains constant up to about 450 K, at which point the sulfur coverage generated through thiolate decomposition is about 0.009, suggesting that adsorbed sulfur does not measurably inhibit the direct reaction up to this coverage. Above 450 K, the slope in Figure 6 begins to increase. This indicates that the rate of the reaction(s) generating *tert*-butyl thioalcohol *is rising more quickly than is consistent with the activation energy derived from the leading edge*. This cannot be attributed simply to a rate enhancement due to sulfur which, given the observed change in the leading edge for decomposition between clean and sulfur-modified surfaces, clearly inhibits the direct reaction. A more reasonable explanation is that a second and higher activation energy channel has opened up for *tert*-butyl thioalcohol evolution. The temperature at which the reaction kinetics change also corresponds to the point at which $H_2S$ desorption sets in, and these observations are nicely explained by the onset of reactions 3, 4, 5, and 6 involving sulfur as a reactant in competition with reaction 1. The rate of $H_2S$ evolution gives very rapidly, indicating that it formed via a high activation energy/high preexponential process in competition with a lower activation energy/lower preexponential process. The disproportionation of SH groups to form $H_2S$ (reaction 5) has an activation energy in the range 39–49 kJ mol$^{-1}$ but will compete poorly because it is second order in SH and also has a low preexponential factor.[6] If reaction 5 were responsible for most of the $H_2S$ desorption, in competition with reaction 6, then a slowly varying leading edge for $H_2S$ desorption and a slowly varying trailing edge for *tert*-butyl thioalcohol desorption would be expected because of the low activation energies and preexponential factors for both processes, a result inconsistent with observation. Reactions 3 and 4 appear instead to be rate-determining.

It is also of interest to compare the reactions and mechanisms proposed here to those observed in organometallic systems.[31–35,58] The most common reaction observed for thiolate ligands at transition metal centers is C–S bond cleavage to yield alkanes (or benzene derivatives) and coordinated sulfur. Reductive elimination involving a coordinated hydrogen ligand and loss of an alkyl/aryl radical into the solution phase followed by hydrogen abstraction have both been proposed as possible mechanisms. This reaction has no real analogy in the Au(110)/thiolate system because no hydrogen is present on the surface in the temperature regime for C–S bond cleavage. Benzyl thiolate conversion to dibenzyl has also been observed, but again attributed to recombination of solution-phase radical species.[64] Formation of alkenes from the disproportionation of sterically hindered alkyl thiolate or sulfides has been observed, but the mechanism was attributed to the loss of alkyl radicals to the solution phase followed by hydrogen transfer between radical species.[65] Ethyl and phenyl thiolates decomposition on Au(110) leads to sulfide formation, and this reaction has also been observed in some homogeneous systems.[66,35]

Studies of organometallic/thiolate systems have concentrated on these most active in the C–S bond reduction. It is possible that homogeneous gold/thiolate systems might show similar chemistry to the Au(110)/thiolate system; however, the geometric constraints against reaction at a single metal center will be severe. We believe that the reactions we observe may be unique to noble metal surfaces.

## 4.5. The Chemistry of *tert*-Butyl Thioalcohol versus *tert*-Butyl Alcohol.

Alkyl alcohols adsorbed on clean Ag and Au surfaces adsorb and desorb purely molecularly;[2–5] no O–H bond cleavage occurs. This behavior can be correlated with the greater O–H bond strength compared to S–H.[46,67] On oxygen precovered surfaces, however, alkoxides are formed by reaction with adsorbed atomic oxygen. We observe the analogous reaction between thiols and adsorbed sulfur on both Ag(110) and Au(110), in addition to the S–H bond cleavage observed on the clean Au(110) surface. Primary and secondary alkoxides on Ag(110) and Au(110) react to form an aldehyde or ketone, by loss of a hydrogen $\beta$ to oxygen. This process will be more difficult in adsorbed thiolates because C(2p)–S(3p) $\pi$ overlap is much less efficient than C(2p)–O(2p) $\pi$ overlap. The consequence of good overlap in alkoxides is that the C–H bond is significantly easier to cleave because the transition state is stabilized by the adjacent oxygen atom; in sulfur-based systems, much less C–H bond weakening occurs.[68] C–O single bonds are also stronger than C–S single bonds[67,69] and thus tend to remain intact in alkoxide decomposition on silver and gold; in contrast, we observe extensive C–S bond cleavage in thiolates adsorbed on Au(110) and Ag(110).

In particular, the reactivity of *tert*-butyl thioalcohol can be compared with the reactivity of *tert*-butyl alcohol on clean and atomic oxygen covered Ag(110) surfaces.[2] *tert*-Butoxy species are formed at low temperature on Ag(110) through reaction with atomic oxygen. Since *tert*-butyl alcohol is a tertiary alcohol, ketone formation through loss of $\beta$-H does not occur. *tert*-Butoxy species decompose around 500 K to form a mixture of isobutene, isobutene oxide, and *tert*-butyl alcohol, and two distinct reaction channels have been suggested. One channel is equivalent to reaction 1 proposed here and has been attributed to the direct reaction of two *tert*-butoxy species to form *tert*-butyl alcohol and an intermediate which can decompose to either isobutene or isobutene oxide. The alternative process, which occurs at lower temperature, is attributed to an oxygen-assisted process, yielding water and isobutene (or isobutene oxide), and equivalent to reactions 3 and 4/5 above. Since no *tert*-butyl alcohol is produced via the oxygen assisted channel, it seems that OH does not react with *tert*-butoxy species to yield *tert*-butyl alcohol and adsorbed oxygen, a reaction analogous to (6) here. Relative gas-phase acidities have been found to be good predictors of reactivity in oxygen-based systems on Ag(110) surfaces. The following values have been determined for $\Delta G_{acid}$ (kcal mol$^{-1}$): *t*-BuO–H, 368.0; H–O·, 376.3; HO–H, 384.1.[70] These values predict that adsorbed *tert*-butoxy species are insufficiently basic to extract hydrogen from OH to form *tert*-butyl alcohol, consistent with absence of the reaction channel equivalent to (6) here. Gas-phase acidities also rationalize the relative ease and lower temperature for the reaction channel involving the attack of adsorbed oxygen on $\gamma$-H to form isobutene (and isobutene oxide) compared to the reaction channel involving attack by the *tert*-butoxy oxygen on the same $\gamma$-H atom, since the former is much more basic. The converse seems to be true in the sulfur system, where the reaction observed first on the sulfur-free Au(110) surface is the thiolate + thiolate reaction, with the reactions involving adsorbed sulfur atoms having the higher activation energy. *In general, reactions involving sulfur correlate poorly with predictions based on gas-phase acidities.*[71]

## 5. Conclusions

*tert*-Butyl thioalcohol adsorbed on clean and partially sulfided Au(110) surfaces undergoes S–H bond cleavage between 100 and 350 K during TPRS to form adsorbed *tert*-butyl thiolate, in

(61) A plot of this type assuming a process first order in thiolate also appears linear, with a similar activation energy. The linearity is, therefore, no confirmation of mechanism, but a distinct break in the plot is seen at the same point, however.

(62) Compared to the effect of sulfur on adsorbed SH[5] and the effect of adsorbed oxygen on adsorbed hydroxide.[63] In both cases the activation energy for disproportionation to $H_2X$ and X is increased by coverage of X.

(63) Jorgensen, S. W.; Sault, A. G.; Madix, R. J. *Langmuir* **1985**, *1*, 526.

(64) Adams, R. D.; Horvath, I. T.; Mathur, P.; Segmueller, B. E. *Organometallics* **1983**, *2*, 996.

(65) Ng, C. T.; Wang, X.; Luh, T.-Y. *J. Org. Chem.* **1988**, *53*, 2536.

(66) Tatsumi, K.; Sekiguchi, Y.; Nakamura, A.; Cramer, R. E.; Rupp, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 1358.

(67) *CRC Handbook of Chemistry and Physics*, 72nd ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1991; p 9–114.

(68) Shum, L. G. S.; Benson, S. W. *Int. J. Chem. Kinet.* **1983**, *15*, 433, 941.

(69) Benson, S. W. *Chem. Rev.* **1978**, *78*, 23.

(70) Defined as the free energy required for the reaction BH → B$^-$ + H$^+$. For values, see: *The 1987 Gas Phase Acidity Scale*, collated by John Bartmess, University of Tennessee.

(71) Jaffey, D. M.; Madix, R. J. Unpublished work.

competition with the desorption of molecularly adsorbed thiol. $H_2$ and $H_2S$ evolution is seen over this temperature range also, and $H_2S$ formation is attributed to a *direct* reaction between the thiol and adsorbed sulfur, rather than to the recombination of adsorbed atomic hydrogen and sulfur. *tert*-Butyl thiolate is stable to above 400 K and decomposes to evolve isobutene, *tert*-butyl thioalcohol, and $H_2S$ into the gas phase. Direct disproportionation reactions between adsorbed thiolate and adsorbed sulfur or a second thiolate group are proposed.

## Appendix

In earlier work we determined the monolayer coverage of $H_2S$ on Au(110) to be $0.77 \pm 0.04$.[6] Using the mass spectrometer sensitivity factor for $H_2S$ obtained through the calibration, we were able to quantify the absolute coverages of $H_2S$ which desorb here and hence the absolute coverages of *tert*-butyl thiolate generated and also the amounts of the different products formed from the thiolate. We assumed that *tert*-butyl thiolate was the only species formed from *tert*-butyl thioalcohol adsorption and hence that the amount of adsorbed thiolate generated on the surface is equal to twice the sum of the amounts of $H_2S$ and $H_2$ that desorb below 350 K. The amount of adsorbed thiolate formed is also equal to the sum of the amounts of *tert*-butyl thioalcohol and isobutene which desorb above 400 K. In addition, the difference between the amount of isobutene and the amount of *tert*-butyl thioalcohol that desorbs above 400 K must also be equal to twice the amount of $H_2S$ and $H_2$ that desorbs above 400 K. Six separate adsorption experiments were performed sequentially and, using the data from these six experiments together with the above constraints, a set of six simultaneous equations were generated, from which can be determined sensitivity factors to convert the measured desorption areas of $H_2$, *tert*-butyl thioalcohol, and isobutene to absolute coverages. Because of the inevitable inaccuracy in the measurement of individual desorption areas, we can only characterize the values we determine as best fit values. The predicted variation in surface sulfur coverage is consistent with the experimental measurements.