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Reactivity of Sulfur-Containing Molecules on Noble Metal Surfaces. 4. Benzenethiol on Au(110)

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Abstract: The adsorption of benzenethiol on clean and sulfided Au(110) surfaces has been investigated with temperature programmed reaction spectroscopy. The monolayer is saturated at an benzenethiol coverage of 0.25 monolayers. About one-half of the thiol adsorbed at 100 K undergoes S–H bond cleavage below 300 K to form phenyl thiolate; H_2 and H_2S are evolved between 150 and 350 K. Phenyl thiolate decomposes above 400 K on clean Au(110) to yield mainly biphenyl, together with diphenyl sulfide, benzenethiol, and dibenzothiophene. With sulfidation of the Au(110) surface, the yield of biphenyl drops, while that of diphenyl sulfide rises. The range of products formed arises from competing C–S bond cleavage and C–H bond cleavage processes.

1. Introduction

This paper is part of a series discussing the adsorption and decomposition of sulfur-containing molecules on the Au(110) surface. In other papers in the series, the adsorption of H_2S,[1] *tert*-butyl thioalcohol,[2] and ethanethiol[3] are discussed. Our interest in the behavior of such molecules on gold surfaces stems from the use of gold thin films as sensors for these species.[5] A measurable change in gold film resistance occurs on exposure to H_2S and other molecules, but the adsorbed species responsible for the change in film resistance have not been characterized. This work was motivated by the potential for developing chemically specific sensors based on reactivity differences.

The adsorption of sulfur-containing molecules such as alkyl and aryl thioalcohols and sulfides has been previously studied on a number of surfaces such as Mo(110),[5–11] Cu(100),[12] Pt(111),[13,14] Ni(110),[15,16] Ni(111),[17] Ni(100),[18] Fe(100),[19] and W(211).[20] S–H bond cleavage is generally facile at 100 K, and C–S bond cleavage frequently occurs below 300 K. It is only relatively recently that the reactivity of thiol, thiolate, and organic sulfide ligands in transition metal complexes has been studied in any detail; this is due, at least in part, to the ease with which S–H bond and C–S bond cleavages occur in these systems.[11,21–25] In contrast, on gold surfaces, S–H bond cleavage occurs incompletely in competition with desorption of the molecular species,[1–3,26,27] and C–S bond cleavage occurs only at 400–600 K, depending on the molecule involved and the surface sulfur coverage. High coverages of thiolates can be achieved on gold surfaces by adsorption from solution where tremendously high exposures can be achieved.[28–31] In this paper we discuss the study of adsorption and decomposition of benzenethiol on Au(110) using temperature programmed reaction spectroscopy (TPRS). As in our previous work, we observe thiolate formation via S–H bond cleavage between 100 and 350 K, activated by either the Au(110) surface or by adsorbed sulfur; above about 450 K, phenyl thiolate decomposes to form benzenethiol, biphenyl, diphenyl sulfide, and dibenzothiophene, depositing sulfur and a small amount of hydrocarbon residue.

2. Experimental Techniques

The experiments reported here were performed in a stainless steel ion-pumped ultrahigh vacuum chamber with a base pressure of 8×10^{-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 reaction (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 about 100 K via a liquid nitrogen reservoir and radiatively heated to above 700 K. Surfaces were cleaned using previously established procedures.[2] Gases were dosed onto the surface 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 to lie about 5 mm from the 3-mm-diameter hole in the QMS collimator and heated at a typical rate of 10 K s^{-1}. The temperature was measured using a chromel–alumel thermocouple pressed tightly against the crystal. TPRS experiments were performed with the crystal biased at −90 V relative to ground to

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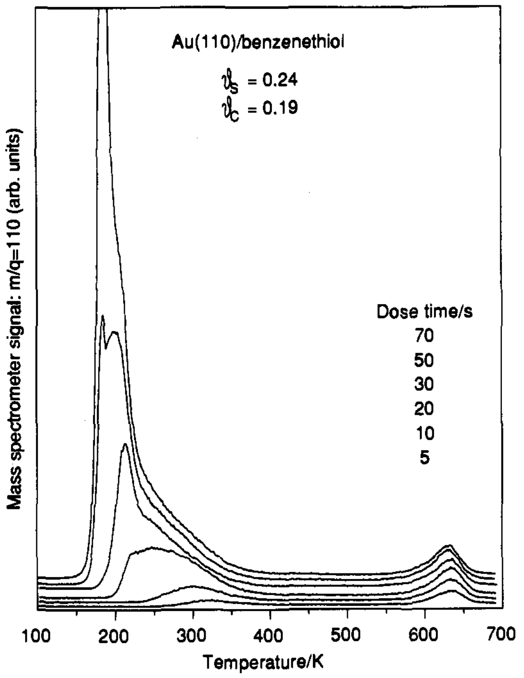

Figure 1. Benzenethiol desorption spectra for the uptake of benzenethiol onto a previous explosed Au(110) surface at 95 K. Relative exposures as shown on the figure.

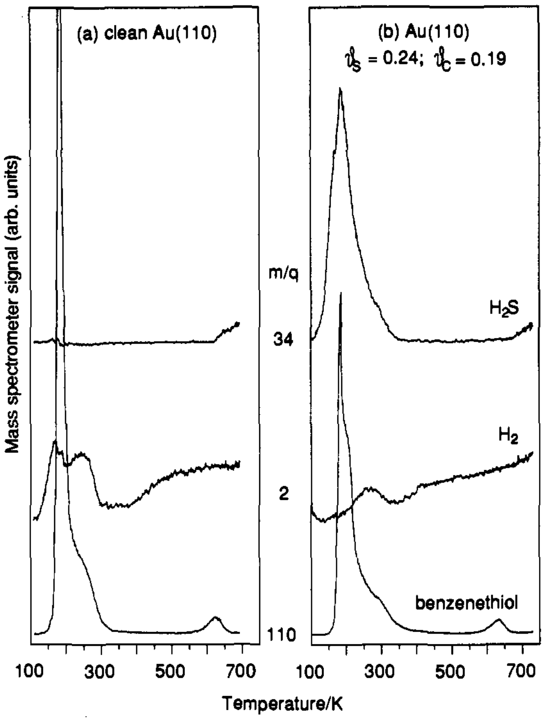

Figure 2. Temperature programmed reaction spectra for benzenethiol adsorbed onto (a) clean and (b) previously exposed Au(110) surfaces, showing the changes in benzenethiol, H_2, and H_2S evolution. Traces have been corrected for the cracking of higher molecular weight species.

prevent electron beam induced decomposition of adsorbates, 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. Benzenethiol (Aldrich, 99+% liquid purity) was purified daily before use by a series of freeze–pump–thaw cycles. Further benzene was removed by pumping on the vapor above the liquid at room temperature. Any small amounts of benzene there are dosed are anticipated to adsorb and desorb reversibly on Au(110), as happens on Ag(110) below 300 K.[32] The dosing lines were largely passivated toward benzenethiol decomposition by repeated exposure to benzenethiol and H_2S.

3. Results

3.1. Desorption below 400 K. Typical desorption spectra for benzenethiol adsorbed onto an Au(110) surface are shown in Figure 1. The absolute exposures to benzenethiol and absolute coverages are unknown, with relative doses given only by dose time. The surface in this case had been previously exposed to benzenethiol and therefore had a partial coverage of both sulfur and carbon. A number of different desorption states are evident between 200 and 350 K, corresponding to activation energies for desorption of between 49.1 and 81.1 kJ mol^{-1}.[33,34] Multilayer desorption occurs at around 190 K. This temperature corresponds to an activation energy for desorption of about 46 kJ mol^{-1},[35] which is close to the enthalpy of vaporization of benzenethiol of 47.56 kJ mol^{-1}.[36] In addition to these desorption-limited states, benzenethiol was also evolved from the surface above 550 K together with a number of other different species via surface reaction-limited processes; these are discussed in the following section.

The desorption of chemisorbed benzenethiol is accompanied by H_2 evolution on an initially clean Au(110) surface and by a mixture of H_2 and H_2S on a surface previously exposed to benzenethiol (Figure 2). Peaks for H_2 evolution are seen on the surface free of sulfur and hydrocarbon at 175 and 250 K. On the clean and sulfided Au(110) surfaces, H_2 has been found to desorb recombinatively at about 215 K.[1] The H_2 at 175 K desorbs alone; no other products are observed at this temperature. We therefore attribute the lower state to a desorption-limited process, with the peak temperature for H_2 desorption decreased because of the higher effective local hydrogen atom coverage due to the presence of surface thiolate. The alternative explanation, that the S–H bond is activated at 175 K and H atom recombination occurs immediately, is less likely, but absolute proof awaits a spectroscopic study. We attribute the higher temperature state to a surface reaction-limited process, which occurs along with further benzenethiol desorption at the same temperature—evidenced by the shoulder on the thiol trace. H_2S has previously been observed to desorb from a sulfided Au(110) surface from 100 to 320 K.[1] The desorption states above 270 K were attributed to the disproportionation of adsorbed SH groups, and therefore, H_2S evolution accompanying benzenethiol desorption may involve a mixture of desorption-limited molecular H_2S evolution and reaction-limited processes involving SH groups.

3.2. Identification of Products Desorbing above 500 K. Above 500 K, a number of different species are evolved from the surface. The species were identified by monitoring all mass fragments between $m/q = 30$ and 300. The major fragments associated with each desorption feature were compared to published cracking patterns for all of the likely products of phenyl thiolate decomposition (Figure 3), as shown in Table 1.[37,38] On the basis of these cracking patterns, the various products can be identified unambiguously.[39,40] Relative fragment intensities were all consistent with the published cracking patterns.

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[33] Activation energies were calculated using Redhead's equation,[34] and a preexponential factor of 10^{13} s^{-1} was assumed.

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[39] Masses between 50 and 80 were unhelpful in general for product identification because most of the fragments in this mass range can be formed from all of the molecules, albeit in rather different relative intensities. However, having identified the various products via their high m/q fragments, the spectra for lower masses such as 77 and 51 were checked to see that they did indeed consist of appropriate convolutions of the higher mass spectra.

Table 1. Published Cracking Patterns for Some Postulated Products of Phenyl Thiolate Decomposition on Au(110)

benzenethiol		benzene		diphenyl sulfide		biphenyl		biphenylene		thianthrene		dibenzothiophene		diphenyl disulfide	
m/q	%	*m/q*	%	*m/q*	%	*m/q*	%	*m/q*	%	*m/q*	%	*m/q*	%	*m/q*	%
110	100	**78**	100	**186**	100	**154**	100	**152**	100	**216**	100	**184**	100	**109**	100
66	35	52	18	185	49	153	35	151	26	**184**	58	185	14	**218**	87
109	24	51	16	51	25	**152**	25	153	16	69	23	**139**	13	65	39
84	16	77	17	**184**	22	76	21	76	15	217	15	92	11	**110**	33
51	17	50	13	187	15	155	14	150	14	**171**	15	79	5	69	19
39	15	39	13	77	14	77	9	63	12	45	13	186	5	**154**	17
77	14	79	7	65	9	151	8	**126**	9	108	13	**152**	5	39	16
50	14	76	5	39	9	51	8	75	8	**139**	12	183	4	77	14
65	13			92	8	64	7	74	7	50	10	69	3	51	14
69	13					63	6			39	10			185	14

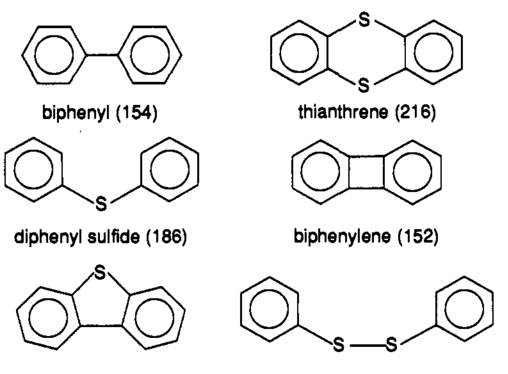

Figure 3. Chemical structures of some postulated products of phenyl thiolate decomposition.

On the basis of the cracking patterns, distinct fragments were chosen to monitor each product. Benzenethiol was characterized by the presence of $m/q = 110$. Diphenyl sulfide was identified by the presence of $m/q = 186$. Biphenyl was monitored at $m/q = 154$. Biphenylene was searched for at $m/q = 152$ in the absence of $m/q = 154$. Thianthrene and dibenzothiophene can only be distinguished on the basis of the molecular ion of thianthrene at $m/q = 216$, since the two share many cracking fragments. The observation of $m/q = 184$ in the absence of $m/q = 216$ (and, of course, in the absence of $m/q = 186$ due to diphenyl sulfide) was taken to indicate the evolution of dibenzothiophene.[41] Diphenyl disulfide was identified by the presence of $m/q = 218$ and/or excess amounts of $m/q = 109$ over that expected to accompany $m/q = 110$ for benzenethiol.[42]

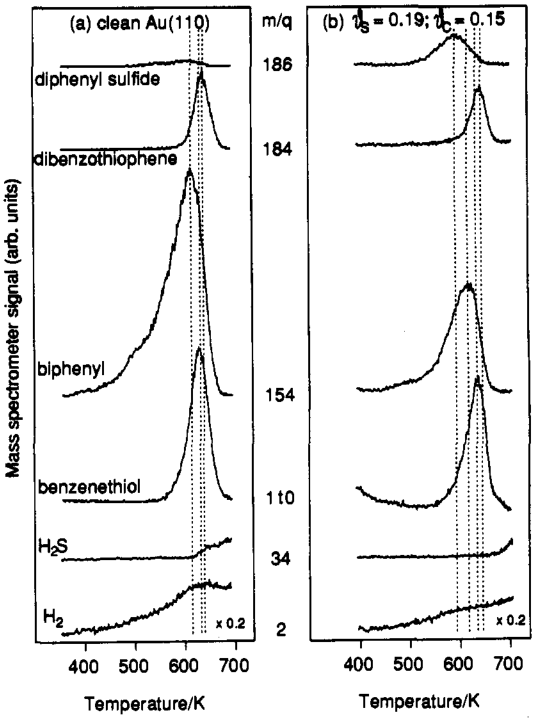

Figure 4. Temperature programmed reaction spectra for the evolution of products from phenyl thiolate decomposition: $m/q = 2$ (H_2); $m/q = 34$ (H_2S); $m/q = 110$ (benzenethiol); $m/q = 154$ (biphenyl); $m/q = 184$ (dibenzothiophene); $m/q = 186$ (diphenyl sulfide). Adsorption onto (a) clean Au(110) and (b) previously exposed Au(110). Where possible, traces have been corrected for the cracking of higher molecular weight species.

On the basis of this analysis, the following products were identified: benzenethiol (630–635 K), biphenyl (615–619 K), dibenzothiophene (638–645 K), and diphenyl sulfide (594 K). On one occasion, $m/q = 216$ was observed, coincident with dibenzothiophene, with an intensity about 2% of $m/q = 184$, suggesting that a small amount of thianthrene was formed. On a surface with a sulfur precoverage of $\theta_S = 0.2$ (but no carbon residue), diphenyl disulfide desorption was identified via a peak in the mass spectrum ($m/q = 109$) at 491 K (no $m/q = 110$), but this state was not observed on clean surfaces or on surfaces that had been previously exposed to benzenethiol. No biphenylene was ever observed. Typical TPRS traces in the temperature range above 500 K are shown in Figure 4 for benzenethiol adsorption on both clean (a) and preexposed (b) Au(110) surfaces. No H_2S desorption is observed in either case, except for a small rising edge above 650 K, which may correspond to decomposition of the adsorbed residue or to desorption from the crystal mount. Some $m/q = 2$ was detected. Whether this corresponds to cracking of the various organic species or to the evolution of molecular hydrogen itself is not known. If it corresponds to molecular H_2, the amount involved is at most only about 2% of the phenyl thiolate coverage.

Evidence that the species evolved above 500 K are indeed the result of decomposition rather than contaminant species dosed along with benzenethiol at 100 K comes from a consideration of the variation in the yield of these species with the amount of

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(40) A significant amount of $m/q = 78$ was observed in the spectrum of fragments associated with benzenethiol desorbing via the multilayer desorption peak at 190 K. Since 78 is neither a part of the published cracking patterns of benzenethiol nor a likely *cracking* fragment, its presence in this state is best attributed to benzene formed by the reaction of benzenethiol on hot surfaces inside the collimating can surrounding the mass spectrometer ionizer. Similar effects have been seen for *tert*-butyl thioalcohol (isobutene and H_2S are observed as apparent cracking fragments of *tert*-butyl thioalcohol[2] and ethanethiol (ions due to ethylene and H_2S are observed).[3] Since the adsorption behavior of the various decomposition products themselves was not investigated, we do not know which molecules will generate $m/q = 78$ in the mass spectrometer. However, given that benzenethiol generates benzene, it is likely that benzene will also be formed in the ionizer by diphenyl sulfide, biphenyl, and diphenyl disulfide. Thus when $m/q = 78$ is observed as a cracking fragment of the decomposition products, it is not possible to determine unequivocally whether benzene itself is desorbing coincidentally. Attempts to null the $m/q = 78$ spectrum by subtraction of appropriate fractions of higher molecular weight spectra suggest that some benzene may desorb at 520 K on the sulfur-free surface.

(41) Since the resolution of the mass spectrometer was adjusted to be constant at about 1 amu across the complete mass range and since $m/q = 184$ was readily detected in the mass spectrometer, $m/q = 216$ should also be observed if present.

(42) The cracking pattern of benzenethiol was determined from the fragment distribution in the benzenethiol multilayer desorption peak.

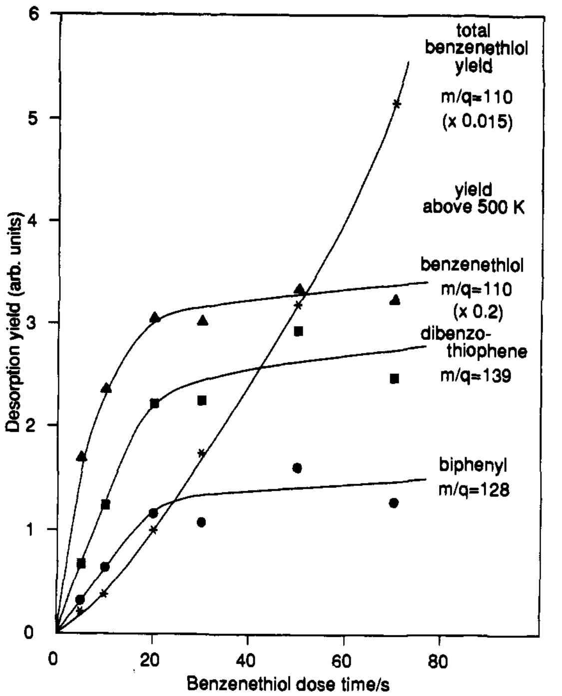

Figure 5. Variation in desorption yield of benzenethiol (m/q = 110), biphenyl (m/q = 128), and dibenzothiophene (m/q = 139) as a function of benzenethiol dose time. Data correspond to the benzenethiol uptake experiment shown in Figure 1.

benzenethiol dosed. None of these species were seen in the mass spectrometer accompanying benzenethiol desorption at low temperature, and hence they are not the result of reactions inside the ionizer. In Figure 5, the yield above 500 K is plotted as a function of benzenethiol dose time for benzenethiol, biphenyl, and dibenzothiophene together with the *total* yield for benzenethiol.[43] It is clear that the yields of biphenyl and dibenzothiophene saturate in the same way as does the yield of benzenethiol for the state above 500 K. If biphenyl and dibenzothiophene were simply being dosed with benzenethiol at 100 K then their yields would be expected to vary in a similar fashion to the total benzenethiol yield, which they clearly do not. The total yield of benzenethiol instead varies approximately linearly with dose time; the deviation from linearity is consistent with our neglect of that fraction of adsorbed benzenethiol which reacts and is evolved as species other than benzenethiol. No data was collected in this particular experiment for diphenyl sulfide; however, the appearance of diphenyl sulfide depends on the presence of surface sulfur (see Figures 4, 6, and 7), again suggesting that it arises as a result of a surface reaction rather than from contaminated benzenethiol. Also, the desorption spectrum of biphenyl from Ag(111) has been recently reported:[44] biphenyl adsorbs purely molecularly on this similarly unreactive surface and desorbs completely below 450 K. The recombination of phenyl fragments to desorb as biphenyl occurs in the same temperature range in the presence of chlorine.[45] We conclude that biphenyl and the other species observed are the products of surface reaction-limited processes occurring on the Au(110) surface.

After exposure to benzenethiol and flashing of the surface to 700 K, both carbon and sulfur were left behind on the surface. The coverages of sulfur and carbon were both measured after a number of adsorption/desorption experiments by AES (Figure 8). Sulfur coverages were quantified by comparison to results for the adsorption of *tert*-butyl thioalcohol[2] and H_2S[1] on the

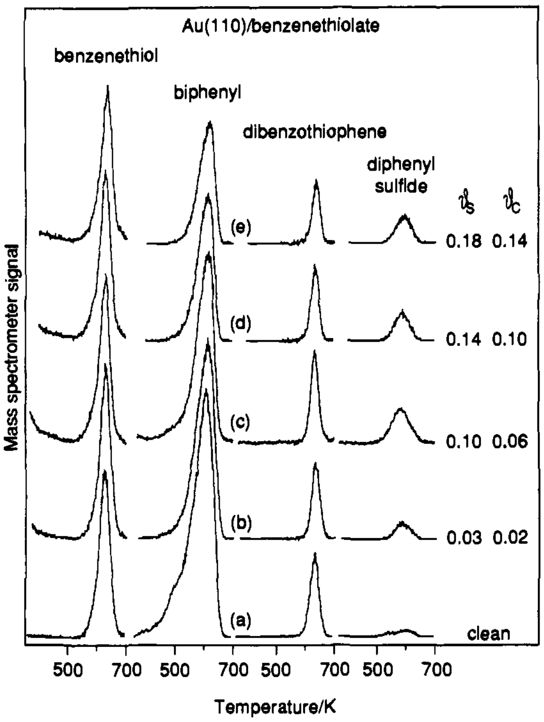

Figure 6. Temperature programmed reaction spectra for benzenethiol, biphenyl, dibenzothiophene, and diphenyl sulfide during a series of repeated multilayer exposures to benzenethiol on an initially clean Au(110) surface. Sulfur and carbon coverages shown have been estimated from Figure 8, except for (e) where from experiment.

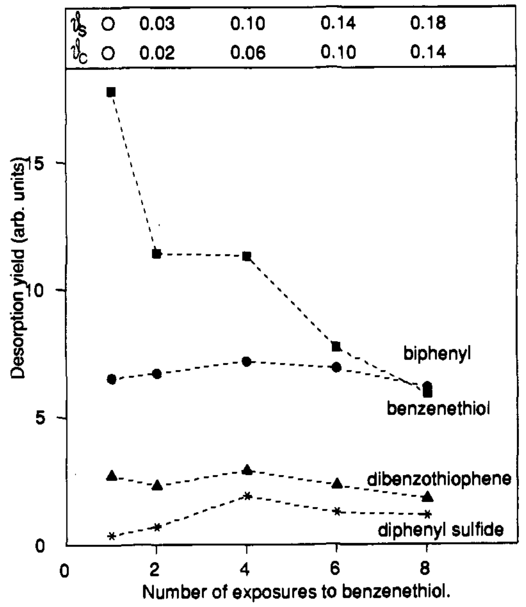

Figure 7. Variation in desorption yield for the various products of phenyl thiolate decomposition during a series of repeated exposures to benzenethiol of initially clean Au(110).

same surface, and carbon coverages were calculated from relative carbon and sulfur Auger peak heights on the basis of published sensitivity factors.[46] The surface sulfur coverage rises rapidly initially and then appears to approach saturation. In contrast, the surface carbon coverage increases linearly with repeated dosing of benzenethiol. In two separate experiments involving the adsorption of several multilayers of benzenethiol onto a clean Au(110) surface, it was found that a sulfur coverage (θ_S) of 0.11 ± 0.02 monolayers was deposited,[47] rising to a value of about 0.3 with repeated dosing. Not all of this sulfur is likely to be present

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[43] Different masses were used in this experiment because the computer control was configured to permit only m/q values below 150.

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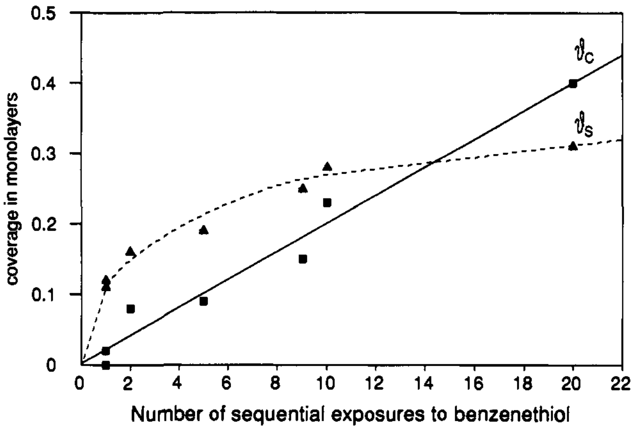

Figure 8. Variation in surface sulfur and carbon coverages for repeated adsorption of multilayer coverages of benzenethiol on Au(110) followed by TPRS, as determined by AES: (—) straight line fit to θ_C data; (- - -) line drawn through θ_S data to aid eye.

as atomic sulfur (see below). The amount of carbon deposited by exposure to a single multilayer dose of benzenethiol was estimated to be about $\theta_C = 0.02$. This corresponds to a phenyl ring coverage of only about 0.003. The difference between the buildup of sulfur and of carbon arises for several reasons. First, sulfur is initially deposited rapidly through C–S cleavage and biphenyl formation; second, sulfur is removed from the surface as H_2S by reaction with benzenethiol below 350 K, while the deposition of carbon is irreversible; third, the amount of sulfur deposited through phenyl thiolate decomposition drops strongly with successive exposures as the amount of biphenyl generated is reduced, leading to a limiting sulfur coverage of about 0.3 (Figure 8).[48]

4. Discussion

4.1. Phenyl Thiolate Formation. As for *tert*-butyl thioalcohol[2] and ethanethiol,[3] we attribute the desorption of H_2 and H_2S to the formation of adsorbed thiolate species, through the activation of adsorbed benzenethiol by both the clean and sulfur-modified Au(110) surfaces. The amounts of H_2 and H_2S that desorb can be used to quantify the amount of phenyl thiolate formed, using conversion factors determined previously.[1] On a Au(110) surface initially free of sulfur, a multilayer coverage of benzenethiol generates a fractional thiolate coverage, θ_{th}, of 0.16 ± 0.02.[47] On subsequent heating and continued exposures to multilayer doses of benzenethiol, the amount of phenyl thiolate formed progressively decreases, falling to $\theta_{th} = 0.12$ on the eighth exposure at a sulfur coverage of 0.18.

The maximum coverage possible for a monolayer of benzenethiol or phenyl thiolate adsorbed on the Au(110) surface can be estimated on the basis of van der Waals dimensions[49] for various adsorption geometries. For adsorption with the aromatic ring parallel to the surface, a maximum coverage of 0.2 is calculated, while the maximum possible coverage of benzenethiol is about 0.4. For phenyl thiolate, the maximum monolayer coverage possible is 0.47, corresponding to a linear C–S–Au geometry. On Au(110) the phenyl thiolate coverage is clearly low enough to accommodate a geometry in which the phenyl ring is parallel to the surface. For comparison, at low coverages of phenol and phenoxide adsorbed on Ag(110), the ring is tilted only about 20° away from the surface plane.[32]

Benzenethiol adsorption has been previously investigated on only a few surfaces. Benzenethiol was found to adsorb with S–H bond cleavage on Cu surfaces at 300 K,[50] but the further reactions of the phenyl thiolate were not investigated. On Mo(110), S–H bond cleavage occurs on adsorption at 120 K.[6] For low exposures (i.e. relatively clean surfaces), complete decomposition occurs to give dihydrogen as the only desorbing product. On a surface partially deactivated by the presence of adsorbed sulfur and carbon, phenyl thiolate can be isolated as an intermediate, stable to about 250 K. In the presence of adsorbed hydrogen, C–S bond hydrogenolysis occurs to yield gas-phase benzene. Phenyl groups are apparently not formed as a long-lived intermediate, since benzene evolution occurs at the same temperature at which atomic sulfur is first detected in XPS. As the surface hydrogen coverage falls, this decomposition route disappears and instead adsorbed benzyne forms and decomposes above 600 K. Similar behavior is observed for benzenethiol adsorbed on the Ni(110) surface.[16] The evolution of benzene from the surface at 200 K is attributed to a hydrogenolysis mechanism, in which hydrogen addition and C–S bond cleavage are both involved in the rate-limiting step.

4.2. Phenyl Thiolate Decomposition. From the range of observed products it is clear that there are several reaction pathways for phenyl thiolate. The reactivity of phenyl thiolate differs from that of *tert*-butyl thiolate[2] and ethyl thiolate[3] by the much higher temperature of product evolution (peak temperatures around 600 K instead of around 500 K) and the formation of biphenyl, a "skeletal" recombination product, as a major product on the sulfur-free surface. Biphenyl adsorption has recently been characterized on the similarly unreactive Ag(111) surface; no decomposition occurred, and desorption was complete by about 400 K.[44] Recombinative desorption of phenyl groups as biphenyl after photon-induced C–Cl bond cleavage in chlorobenzene[45] and after electron-stimulated C–H bond cleavage in adsorbed benzene[44] also occurs on Ag(110) at the same temperature. Thus neither biphenyl molecules nor phenyl groups are likely to be stable on the Au(110) surface above 400 K, and the formation of biphenyl on Au(110) near 600 K must involve a surface reaction-limited process at the temperature of evolution. The formation of biphenyl from phenyl thiolate on Au(110) suggests that the reaction mechanism involves C–S bond cleavage to form adsorbed phenyl and sulfur as an initiating step, followed by immediate phenyl group recombination. The peak temperature indicates an activation energy for C–S bond cleavage of approximately 160 kJ mol^{-1}. The formation of diphenyl sulfide can be similarly the result of combination of phenyl groups resulting from C–S bond cleavage in the thiolate with adsorbed thiolate groups.

Accordingly, the formation of diphenyl sulfide competes with biphenyl formation. If C–S bond cleavage were the rate-limiting process in this chain of events and all other reactions proceeded very rapidly thereafter, the temperature programmed reaction profiles for biphenyl and diphenyl sulfide should coincide. In fact, the maximum rate for diphenyl sulfide precedes that for biphenyl, even though biphenyl production is initiated before that of diphenyl sulfide. These results can be explained by the following sequence of reactions:

$$C_6H_5S_{(a)} \rightarrow C_6H_{5(a)} + S_{(a)} \tag{1}$$

$$2C_6H_{5(a)} \rightarrow C_{12}H_{10(g)} \tag{2}$$

$$C_6H_5S_{(a)} + C_6H_{5(a)} \rightarrow C_6H_5SC_6H_{5(g)} \tag{3}$$

The rate constant for reaction 2, k_2, exceeds k_3, and therefore biphenyl *appears* before diphenyl sulfide in the temperature programmed reaction spectrum. The rate of diphenyl sulfide production *peaks* prior to that of biphenyl, however, as the supply of adsorbed thiolate groups is exhausted as the result of reactions 1 and 3. On the sulfur-predosed surface, the presence of sulfur

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[47] Coverages are defined relative to the Au(110) surface atom density of 8.54 × 10^{14} cm^{-2}.

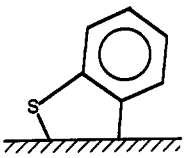
[48] It is interesting to note that the final slow rate of increase in surface sulfur coverage matches the rate of increase in phenyl ring coverage ($=\theta_C/6$), suggesting that the amount of *atomic* sulfur has ceased to increase.

[49] Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

[50] Agron, P. A.; Carlsson, T. A.; Dress, W. B.; Nyberg, G. L. *J. Electron Spectrosc. Relat. Phenom.* **1987**, *42*, 313.

retards the formation of biphenyl somewhat, thereby enhancing the reaction of phenyl groups with surrounding thiolate, favoring the production of diphenyl sulfide.

The evolution of benzenethiol near 630 K is not easily explained. The generation of benzenethiol from the thiolate requires a source of hydrogen. The simultaneous formation of dibenzothiophene suggests a hydrogen transfer reaction between thiolates to form I, as shown below, which may then act as a precursor for dibenzothiophene. The absence of appreciable amounts of dihydrogen or hydrogen sulfide at the temperature at which benzenethiol is generated is strongly suggestive of direct hydrogen transfer to form I by γ-hydrogen abstraction.[51] The temperature at which benzenethiol is regenerated from the thiolate is much higher than that observed for alkyl thioalcohols and correlates well with the higher γ-C–H bond energy, 461 kJ mol^{-1} as compared to 420 kJ mol^{-1}.[52]



I

The possible formation of I is interesting compared to the behavior of phenyl thiolate on Mo(110), where surface benzyne has been identified as an intermediate in phenyl thiolate decomposition.[6] Indeed, C–S bond cleavage in I could lead to benzyne formation on the gold surface also. Dibenzothiophene formation could involve the direct reaction of two I species, with the elimination of sulfur, or the reaction of adsorbed benzyne and I intermediates. The absence of biphenylene among the products—expected from the recombination of benzyne—suggests the former route to be more likely and, indeed, is strongly suggestive of the existence of I. It is importnat to note, however, that other coupled states of the thiolate could produce benzenethiol and dibenzothiophene by a more complex rearrangement. The formation of dibenzothiophene, by whatever mechanism, shows how the chemistry of thiolate decomposition is governed by hydrogen availability, as has been previously observed for other metal surfaces and in organometallic systems.[11,21-25]

Reasonable estimates of the product yields were possible. Quantification of the results was complicated by the multiplicity of products with overlapping cracking fragments and the fact that not quite all of the thiolate was converted into volatile products; details of the procedures used in the estimates are shown in the Appendix. The following amounts of product are formed (coverages are quoted in thiolate equivalents): (a) on the clean Au(110) surface, $\theta_{\text{biphenyl}} = 0.11$, $\theta_{\text{diphenyl sulfide}} = 0.017$, $\theta_{\text{benzenethiol}} = \theta_{\text{dibenzothiophene+I}} = 0.02$; (b) on a preexposed surface, $\theta_{\text{biphenyl}} = 0.04$, $\theta_{\text{diphenyl sulfide}} = 0.05$, $\theta_{\text{benzenethiol}} = \theta_{\text{dibenzothiophene+I}} = 0.02$.

Given the mass spectrometer sensitivity factor for benzenethiol itself, we can estimate the quantity of benzenethiol that is adsorbed in the monolayer state initially on both the clean and preexposed surfaces.[53] In both cases we find the sum of reversibly and irreversibly bound benzenethiol to be 0.25 ± 0.03 monolayers. Thus, about half of the benzenethiol adsorbed into the monolayer at 100 K is converted to phenyl thiolate and about half desorbs molecularly.

4.3. Comparisons between the Behavior of Different Thiols Adsorbed on Au(110). *tert*-Butyl thioalcohol,[2] ethanethiol,[3] and benzenethiol all show extensive S–H bond cleavage of the molecularly adsorbed thiol, with both H_2 and H_2S evolving below 400 K. The relative amount of dihydrogen observed in the two desorption-limited states on the surface free of sulfur is comparable for all three thiols, and the fractional conversion of adsorbed thiol to thiolate is about 0.5 for all three thiols. The reactivity of the thiols differs from that of H_2S which shows extremely little decomposition for adsorption onto a clean Au(110) surface,[1] in accord with the higher S–H bond energy for H_2S compared to the thiols.

The overall features of the decomposition of the thiolates on Au(110) are also similar, though there are differences in decomposition temperature and product distribution. For all three thiolates, the decomposition process depends on sulfur coverage; decomposition begins at somewhat lower temperatures on the sulfur-free surface. Decomposition yields adsorbed sulfur in all cases, but carbon only in the case of phenyl thiolate. Before discussing the origins of the observed differences, it is worth summarizing here the major observations in each system. *tert*-Butyl thioalcohol, isobutene, and H_2S are the only significant productts of *tert*-butyl thiolate decomposition. Decomposition occurs with a peak temperature around 470 K, and the peak temperature is not very sensitive to sulfur coverage, though the peak shape is affected by the presence of sulfur. Ethyl thiolate decomposes on a sulfur-modified surface with a peak maximum at 550 K to yield a mixture of ethanethiol, ethylene, and diethyl sulfide; negligible H_2S or H_2 evolution occurs. On a surface free of sulfur, an additional decomposition route is observed at about 450 K, yielding ethylene and ethane, and the route yielding ethanethiol and ethylene occurs at slightly lower temperature. Diethyl sulfide is not formed unless sulfur is preadsorbed. Phenyl thiolate decomposes to give a much wider range of products, including biphenyl, benzenethiol, and diphenyl sulfide and also dibenzothiophene. On the sulfur-free Au(110) surface, decomposition begins around 400 K, with a peak maximum temperature of about 600 K; no H_2S is evolved and negligible H_2 is formed. Preadsorbed sulfur moves the product distribution away from biphenylene and toward diphenyl sulfide and also increases the temperature at which decomposition begins.

The observed differences in behavior between the various thiolates can be understood in terms of a number of factors, namely, the differing C–S bond strengths, γ-C–H bond strengths, thiolate adsorption energies, and reactivity of sulfur in the various thiolates. The decomposition peak temperature varies significantly for the three systems studied, and it correlates well with the C–S bond strength,[54] which increases from *tert*-butyl thioalcohol to ethanethiol to benzenethiol. The γ-C–H bond strength is also much higher for phenyl thiolate than for *tert*-butyl thiolate and ethyl thiolate.[52] Since C–H bond cleavage is necessary to provide a source of hydrogen to regenerate the parent thiol, it is reasonable that large amounts of thiol are regenerated from *tert*-butyl thiolate and ethyl thiolate, but much less is formed, and that at higher temperature, via a rather different mechanism in the case of phenyl thiolate.

The high γ-C–H homolytic bond energy in benzenethiol also appears to be responsible for the absence of H_2S formation from phenyl thiolate decomposition, since, in essence, H_2S formation requires the cleavage of the C–S bond and two γ-C–H bonds while benzenethiol formation requires the transfer of only one hydrogen atom. A different argument is obviously required to explain the absence of H_2S evolution from ethyl thiolate decomposition, since *tert*-butyl thiolate decomposition *does* lead to H_2S formation. One factor involved must be the higher C–S bond energy in ethyl thiolate compared to *tert*-butyl thiolate, which will affect the branching ratio between competing reactions to favor the formation of ethanethiol and ethylene via intermolecular hydrogen transfer over the formation of ethylene and H_2S via C–S bond cleavage, as is discussed in more detail elsewhere.[3] The higher C–S bond energy in ethyl thiolate and phenyl thiolate as compared to *tert*-butyl thiolate will also favor

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[51] The γ-C-H bond is labeled with respect to the metal center.

[52] McKillen, D. F.; Golden, D. M. *Ann. Rev. Phys. Chem.* **1982**, *33*, 493.

[53] The benzenethiol coverage adsorbed into the monolayer is the sum of the coverage of molecular benzenethiol desorbing above the multilayer, and adding this to the thiolate coverage given by H_2S and H_2 desorption.

[54] Benson, S. W. *Chem. Rev.* **1978**, *78*, 23.

diethyl sulfide and diphenyl sulfide formation relative to di-(*tert*-butyl) sulfide formation. Steric effects due to the bulky *tert*-butyl group will also inhibit di-(*tert*-butyl) sulfide formation. The final point to note on product distribution differences between the thiols is the formation of biphenyl from phenyl thiolate at relatively high temperature; the analogous products are not seen for ethyl thiolate or *tert*-butyl thiolate. The formation of biphenyl seems to reflect the absence of alternative pathways for phenyl thiolate decomposition because of the high γ-C–H bond energy in this system.

The amount of thiolate formed is different for each thiol: ethyl thiolate (0.22–0.24); *tert*-butyl thiolate (0.15–0.18); phenyl thiolate (0.16–0.12). This difference is the consequence of the different monolayer saturation coverages associated with the size of each thiol, since the efficiency of conversion of adsorbed thiol to adsorbed thiolate is comparable for all the thiols. The surface sulfur coverage which develops with repeated exposure to thiol correlates with the thiolate coverage formed for each thiol, except in the case of phenyl thiolate decomposition where the formation of large amounts of biphenyl leads to much higher sulfur coverages.

4.4. Thiolate Decomposition on Au(110) Compared to Other Surfaces. It is clear that decomposition of thiolates occurs at much higher temperatures, and with far more selective chemistry, on Au(110) than on reactive transition metal surfaces[5–20] where nonselective decomposition occurs on the clean surface and hydrocarbon evolution occurs below 400 K. In addition, no sulfur-containing species desorb during TPRS when thiols are adsorbed onto other metals, and this can be attributed to the much stronger interaction between sulfur and metals such as nickel and molybdenum than between sulfur and gold, as indicated by the enthalpies of formation of the sulfides: for example, $\Delta H_f(\mathrm{MoS_2})$ = –116.1 kJ (mol sulfur)$^{-1}$ and $\Delta H_f(\mathrm{Au_2S})$ = +29 kJ (mol sulfur)$^{-1}$.[55,56] One crucial difference in decomposition pathways for the thiolates adsorbed on Au(110) and on other metals so far studied is that adsorbed hydrogen is retained on the metal surface up to temperatures where C–S bond cleavage begins to occur. This allows for the generation of alkanes from alkyl thiolates, or benzene from phenyl thiolate, at temperatures below those required for nonactivated C–H bond cleavage. In contrast, on the Au(110) surface, sulfhydric hydrogen is lost from the surface below 350 K as H_2S and H_2, well below the temperature at which C–S bond cleavage begins. Alkyl thiolates also decompose to form alkenes on Mo(110), but the mechanism is clearly different from that on Au(110) because it is accompanied by H_2 evolution. On metal surfaces other than molybdenum and nickel, only the decomposition of methyl thiolate has been investigated, but analogous chemistry is observed.[10–14,17–20] Methane formation is universal, the mechanism involving a metal-induced C–S bond cleavage of adsorbed methyl thiolate, accompanied by or closely followed by C–H bond formation. The absence of facile C–H bond cleavage on the Au(110) surface means thiolates are kinetically more stable on the gold surface than on more reactive metal surfaces and results in the formation of recombination products not accessible on the Mo(110) surface. On Cu(111),[12] the reactivity of the surface and the H_2 desorption temperature are both sufficiently low that some products other than methane are generated from methyl thiolate, but again the surface affinity for sulfur is such that no sulfur-containing products desorb.

In the one other study that has been performed on thiol adsorption on a gold surface, methanethiol and dimethyl disulfide adsorption on Au(111),[26,27] the results were somewhat different from those found here for the higher molecular weight thiols adsorbed on Au(110). No S–H bond cleavage was observed in adsorbed methanethiol, and dimethyl disulfide, which did undergo S–S bond scission on adsorption to form methyl thiolate, showed purely recombinative desorption. There are several possible explanations for the absence of S–H bond cleavage for methanethiol on Au(111). Clearly, even in the systems that we have studied, S–H bond cleavage is not an easy process and competes with desorption of the thiol. The Au(111) surface may be less active for this reaction than the Au(110) surface *and* adsorb molecular thiols more weakly because of its close-packed surface structure. The coordination number of atoms at the Au(111) surface is nine, while that for atoms at the Au(110) surface is only seven; also the Au(110) surface is known from scanning tunneling microscopy (STM) to be a rather disordered mixture of unreconstructed and reconstructed domains.[57] In support of the suggestion of intrinsic reactivity differences between the two surfaces is the fact that it is slightly harder to sulfide the Au(111) surface than the Au(110) surface using high pressures of H_2S.[58] In combination, these effects may lead to preferential desorption of the molecularly bound thiol from the Au(111) surface. Methyl thiolate adsorbed on Au(111) desorbs purely recombinatively as dimethyl disulfide between about 425 and 500 K, with no formation of dimethyl sulfide. Given that, in the case of ethyl thiolate, diethyl sulfide formation only occurred above about 480 K, and since the C–S bond energy of methyl thiolate is higher than that of ethyl thiolate, purely recombinative desorption of methyl thiolate from a clean Au(111) surface is, therefore, not unexpected. In addition, as discussed above, the Au(110) surface seems to be more active in bond breaking reactions than the Au(111) surface.

In organometallic systems, the only decomposition reactions that have been observed for complexed phenyl thiolate involve the formation of benzene and biphenyl.[21–25] Benzene formation has been attributed to reductive elimination involving a hydrogen ligand, while biphenyl formation was attributed to recombination of dissociated phenyl radicals.

5. Conclusions

The Au(110) surface activates adsorbed benzenethiol toward S–H bond cleavage. However, S–H bond cleavage to form phenyl thiolate is still competitive with molecular benzenethiol desorption during TPRS. Phenyl thiolate groups decompose above about 450 K via three distinct mechanisms to form biphenyl, diphenyl sulfide, and benzenethiol together with dibenzothiophene. The first two of these reactions likely involve C–S bond cleavage as the rate-limiting step, while the last involves C–H bond cleavage. The high activation energy for C–H bond cleavage on the Au(110) surface and the relatively low gold–sulfur bond strength lead to a distinctive chemistry for phenyl thiolate adsorbed on Au(110) as compared to the behavior of phenyl thiolate adsorbed on Mo(110) and other thiolates adsorbed on Au(110).

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Appendix

From previous studies we have determined mass spectrometer sensitivity factors enabling the determination of absolute amounts of H_2S and H_2 desorbing from the Au(110) surface. This enables the phenyl thiolate coverage formed on the surface to be determined. We can generate a set of simultaneous equations to determine conversion factors for the various products to convert from the measured desorption areas to the yield of product in monolayers. For the final set of data shown in Figures 6 and 7, we can generate an equation relating the total phenyl thiolate coverage, given by the amounts of H_2S and H_2 desorption below

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

(56) Puddephatt, R. J. *The Chemistry of Gold*; Elsevier: Amsterdam, 1978.

(57) Binnig, G.; Rohrer, H. Gerber, Ch.; Weibel, E. *Surf. Sci.* **1983**, *131*, L379.

(58) Kostelitz, M.; Domange, J. L.; Oudar, J. *Surf. Sci.* **1973**, *34*, 431.

350 K,[59] to the sum of the desorption areas of the various products, each multiplied by an appropriate mass spectrometer sensitivity factor. If we assume that the amount of **I** plus the amount of dibenzothiophene is equal to the amount of benzenethiol that desorbs (equivalent to assuming that the carbon residue is **I** and that no further H atoms are removed and transferred to form benzenethiol), then we can reduce by one the number of unknowns in the equations. Another equation comes from equating the amount of sulfur that is deposited on the clean surface to the sum of the amount of biphenyl plus one-half the amount of diphenyl sulfide plus one-quarter of the amount of thiolate which follows the route forming benzenethiol. This involves neglecting the amount of sulfur associated with the carbon residue, which is justified since the amount of sulfur associated with the carbon residue equals $(\theta_C)/6 = 0.003$, which is much smaller than the amount of sulfur that is deposited on the clean surface, $\theta_S = 0.11$. From these three equations come mass spectrometer sensitivity factors for benzenethiol, biphenyl, and diphenyl sulfide.

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[59] Conversion factors for H_2S and H_2 come from previous work.[1,2]