

Cyclohexanethiol Adsorption and Reaction on the Ni(111) Surface

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The surface reactions of cyclohexanethiol (CHT) have been characterized on the Ni(111) surface as part of a larger study of C–S bond activation in thiols. The C–S bond is broken by direct interaction with the nickel surface, and hydrogen is primarily involved in subsequent hydrogenation of desulfurized hydrocarbon intermediates. CHT adsorbs at 120 K primarily as cyclohexylthiolate. With heating, C–S bond scission is observed at 240 K evidenced by both sulfur XPS and cyclohexane desorption. Addition of coadsorbed hydrogen does not modify the temperature or extent of desulfurization. A comparison of desulfurization in CHT and benzenethiol indicates that the energetics for C–S bond activation correlate with bond strength, suggesting a radical mechanism. Only a small fraction of the cyclohexane desorbs at 240 K. Most of the gas-phase desulfurized products desorb in a second process starting at 300 K. Cyclohexane is the first product in this second process. Stepwise dehydrogenation of C₆ surface intermediate(s) results in desorption of increasingly dehydrogenated C₆ hydrocarbons with increasing temperature, culminating in benzene desorption at 315 K. Increasing dehydrogenation with increasing temperature is correlated with free hydrogen desorption in this same temperature range. A final disproportionation process in the 450 K range produces a small amount of benzene. With increasing temperature no further gas-phase organics are produced. Overall, about half of the CHT in a monolayer undergoes complete dehydrogenation to form adsorbed carbon and sulfur. For small coverages (<0.07 ML) most of the CHT undergoes complete decomposition on the Ni(111) surface. For these small coverages, no cyclohexane is observed at 240 K, even in the presence of coadsorbed hydrogen. Smaller amounts of C₆ hydrocarbons are formed in the 300–315 K temperature region. It is interesting to note that a small fraction of CHT remains molecular following adsorption at low temperature, producing a CHT peak at 180 K even for low coverages.

Introduction

Desulfurization of sulfur-containing organics plays a key role in a wide range of industrial processes. Mechanisms of these desulfurization processes have been characterized using a variety of approaches.^{1–9} In an effort to develop a molecular level understanding of the key reaction steps involved in desulfurization, surface reactions of a range of organic thiols have been studied on single-crystal metal surfaces. Benzenethiol has been used extensively as a model reactant because of chemical analogies with important complex model sulfur-containing species such as benzothiophene and because of the stability of the C–S bond adjacent to an aromatic ring. A series of previous papers^{10–13} have shown that the C–S bond breaking in benzenethiol does not involve hydrogen for these nickel surfaces. This paper is focused on the effect of replacing the aromatic group in benzenethiol with a saturated C₆ group. Saturating the adjacent C₆ ring weakens the C–S bond and also decreases C–H bond strengths. A combination of TPD and spectroscopic studies has been used to identify key surface reactions observed for CHT in the presence and absence of coadsorbed hydrogen.

The surface reactions of benzenethiol have been previously studied on the Mo(110),¹⁴ Cu(110),¹⁵ Rh(111),¹⁶ Ni(110),¹⁷ Ni(100),^{18,19} and Ni(111)^{10,11} surfaces using UHV methods. Benzenethiol is adsorbed on each of these surfaces as a thiolate with low-temperature (100 K) cleavage of the S–H bond. The steric accessibility of the sulfhydryl hydrogen, taken together with the stability of the H/metal and S/metal bonds, makes thiolate formation favorable for most metals even at low

temperature. The aromatic ring in these thiolates is generally oriented either perpendicular or nearly perpendicular to the surface. On Mo(110),¹⁴ a tilt of 23° away from surface normal was found, while on Pt(111)²⁰ and Ag(111)²¹ surfaces the aromatic ring was found to be perpendicular to the surface. C–S bond activation has been characterized for benzenethiol on the Ni(110) and Ni(100) surfaces. For these surfaces, hydrogen is not involved in the C–S bond activation; rather, direct interaction with the metal surface in the 220–270 K temperature range results in bond breaking. On the Ni(100) surface,¹⁸ the dominant benzene formation pathway for benzenethiol occurs at 270 K. The availability of free hydrogen is limited at reaction temperature by desorption of free hydrogen. Increasing hydrogen availability increases the benzene yield but does not shift the reaction temperature. On the Ni(110) surface benzenethiol¹⁷ forms benzene at approximately 220 K, in a temperature range where hydrogen availability is high. In this case, coadsorbed hydrogen did not influence the benzene yield, and a small temperature decrease related to hydrogen induced reconstruction of the Ni(110) surface was observed.

To provide a basis for comparing the reactivities of cyclohexyl and phenyl thiols, a brief summary of benzenethiol reactivity on the same Ni(111) surface follows. The C–S bond in benzenethiol is broken by direct interaction with the nickel surface at 260 K. The formation of an adsorbed phenyl intermediate is clearly confirmed by studying the reactivity of coadsorbed methanethiol and benzenethiol on the Ni(111) surface.^{12,13} Toluene formation clearly indicates that phenyl and methyl intermediates are formed and couple at 260 K. In the

presence of large amounts of coadsorbed hydrogen, the phenyl intermediate can be hydrogenated to form benzene at the same temperature.^{10,11} Therefore, hydrogen cannot be directly involved in C–S bond breaking. C–S bond activation is independent of surface hydrogen concentration, but the availability of hydrogen increases the yield of benzene at 260 K by hydrogenating the phenyl formed and inhibiting dehydrogenation of surface intermediates. Hydrogenation of adsorbed benzyne, formed by dehydrogenation of phenyl, results in a second benzene peak at 290 K. An additional benzene peak is observed above 350 K from disproportionation of aromatic intermediates.

As potential products of reactions involving a cyclohexyl intermediate, the absorption of cyclohexane and benzene on the Ni(111) surface will be summarized. TPD studies of cyclohexane on Ni(111) have shown that molecular cyclohexane desorbs intact from the Ni(111) surface in the 180–190 K range with no dehydrogenation.^{22,23} Benzene desorbs molecularly from the Ni(111) surface at 191 K.²⁴ In addition, high-temperature hydrogen peaks are observed, indicating that some decomposition of the benzene has occurred.

Little previous research has been reported regarding cyclohexanethiol adsorption and reaction on metal surfaces. CHT adsorbs on Ag(111) through the sulfur atom to form the thiolate.²⁵ The thermal reactions of CHT were not included in previous work. We have found that the mechanism for C–S bond activation is the same in CHT and benzenethiol; however, the general reactivity patterns are significantly different. The C–S bond in CHT breaks in the 240 K range, as indicated by both TPD and XPS, 20 K lower than C–S bond activation in benzenethiol on this same Ni(111) surface. Facile C–H bond activation and increased hydrogen content in CHT results in large hydrogen coverages so that coadsorbed hydrogen does not cause an increase in gas-phase organic product formation following C–S bond scission as observed for benzenethiol on the Ni(111) surface.

Experimental Section

These experiments were performed in a stainless steel UHV chamber described in detail elsewhere¹⁰ with a base pressure of $\sim 1 \times 10^{-10}$ Torr. The Ni(111) sample was mounted on a liquid nitrogen cooled manipulator which could be cooled to 110 K and heated resistively to 1000 K via tungsten support wires. Type K thermocouple wires were spot-welded to the back of the crystal for temperature measurement and control.

Temperature-programmed desorption experiments were performed using a shielded multiplexed quadrupole mass spectrometer. During experiments, the sample was placed within 1 cm of the mass spectrometer ionizer. The heating rate used for all TPD experiments was 5 K/s. XPS was performed with a VSW system and hemispherical analyzer, using a filtered Mg anode.

In all experiments, CHT was purified by several freeze–pump–thaw cycles. Dosing was performed via a directional doser, and exposures are measured in langmuirs (1 langmuir = 10^{-6} Torr s). While the sample received a higher absolute exposure due to directional dosing, relative pressure used in exposure calculation was determined from increases in the chamber background pressure. H₂S was dosed through a separate directional doser and used without further purification. Hydrogen, deuterium, and sputter gases were dosed by back-filling the chamber through a leak valve and were used without further purification. Gas purity was checked frequently by mass spectrometer scans. Thermal reactions of CHT produce no sulfur-containing gas-phase species after removal of the mul-

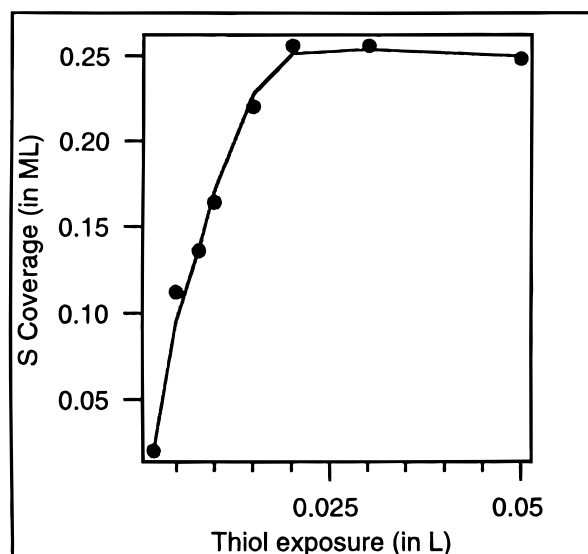


Figure 1. Uptake of sulfur on the Ni(111) surface as a function of CHT exposure. Saturation coverage is achieved at an exposure of 0.020 langmuir of CHT (via directional doser), with a total sulfur coverage of 0.25 ML.

tilayer, allowing the determination of initial thiol coverages based on S(152 eV)/Ni(850 eV) AES ratios.

Results and Discussion

Initial thiol coverages increase with increasing exposure, as indicated by Figure 1. Selected exposures of cyclohexanethiol on the Ni(111) surface were annealed to 800 K, and AES S(152 eV) to Ni(876 eV) peak ratios were determined. These data are converted to an absolute surface coverage by comparison to a S-saturated Ni(111) surface produced by exposure and annealing of H₂S. For annealing temperatures of 800 K, the sulfur saturation of the Ni(111) surface occurs at 0.40 ML and produces a $(5\sqrt{3} \times 2)$ LEED pattern.^{26,27} Based on this value, the thiol saturation coverage from CHT occurs at 0.25 ML, which is consistent with other simple thiols adsorbed on Ni(111),^{28,29} just slightly higher than the saturation coverage of benzenethiol on the Ni(111) surface, which was 0.21 ML.^{10,11} Since the saturation coverage is quite similar to other thiols on the Ni(111) surface, CHT must have a similar surface density. This requires that the CHT be bonded through the sulfur in a largely upright configuration.

The primary desorbing thermal products for the reaction of 0.25 langmuir of CHT on the Ni(111) surface are shown in Figure 2. After the molecular desorption at 180 K, a small cyclohexane peak is observed at 240 K. Cyclohexane formation clearly indicates that the C–S bond in CHT can be broken at this temperature. Comparison of this reactivity data with XPS results discussed later in this section indicates that a desulfurized C₆ cyclic intermediate is formed at this temperature. The low yield of cyclohexane at 240 K indicates that most of the desulfurized surface intermediates are bound strongly to the surface and cannot be hydrogenated by coadsorbed hydrogen at these temperatures. The total gas-phase cyclohexane formed at this temperature accounts for less than 1% of the total adsorbed thiolate.

The majority of gas-phase organic products desorbs at higher temperature. A second cyclohexane peak occurs at 300 K, producing a larger amount of cyclohexane than is observed in the 240 K peak. Free surface hydrogen also begins to desorb in this temperature range. As the amount of surface hydrogen

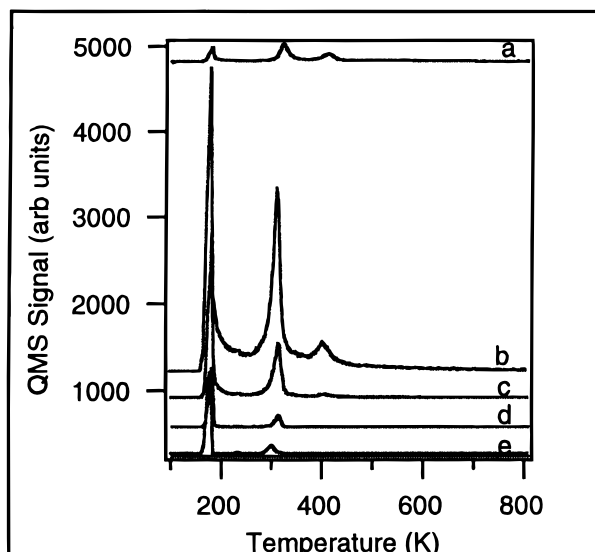


Figure 2. Major products from the thermal reaction of 0.25 ML of CHT on the Ni(111) surface. The curves shown represent (a) hydrogen ($m/e = 2$) \times 0.01, (b) benzene ($m/e = 78$), (c) cyclohexadiene ($m/e = 80$), (d) cyclohexene ($m/e = 82$), and (e) cyclohexane ($m/e = 84$). The 180 K peak is caused by fragmentation of the parent mass, $m/e = 116$.

decreases, dehydrogenation of the remaining surface hydrocarbon intermediates leads to the formation of cyclohexene, cyclohexadiene, and benzene, each at a slightly higher temperature, with the dominant benzene product desorbing at approximately 315 K. The desorption of cyclohexene and cyclohexadiene are clearly reaction limited and are formed by the rapid dehydrogenation of C_6 cyclic intermediates as free hydrogen begins to desorb.

With further increases in temperature, disproportionation and decomposition complete the reactions of CHT on the Ni(111) surface. The final desorbing organic product from CHT reaction on Ni(111) is high-temperature benzene at 400 K. A similar high-temperature benzene peak was observed from benzenethiol on Ni(111)¹¹ and is attributed to the disproportionation of dehydrogenated surface hydrocarbon intermediates. The second hydrogen peak from dehydrogenation of remaining adsorbed hydrocarbons begins at 400 K and extends to 600 K. Complete dehydrogenation and decomposition of the remaining surface species are observed in this temperature range. Above 500 K we observe carbon dissolution into the bulk as expected.³⁰ After annealing to 800 K only sulfur remains on the surface, as evidenced by AES and XPS (not shown).

Cyclohexanethiol surface concentration plays a key role in controlling selectivity during TPD on the Ni(111) surface. The CHT coverage dependence of cyclohexane, and hydrogen are shown in Figures 3 and 4. For the cyclohexane spectra (Figure 3), the temperature scale has been set to eliminate the molecular peak, which has strong fragmentation at $m/e = 84$. At low coverage of CHT, extensive dehydrogenation is observed as indicated by hydrogen desorption at 300 K (Figure 4) and the absence of desorbing cyclohexane (spectrum g, Figure 3). Apparently, a vacant surface available at low coverages facilitates complete dehydrogenation. Extensive dehydrogenation has been observed for low coverages of several other thiols on this Ni(111) surface.^{11,28} The first cyclohexane desorption peak occurs at 300 K for a coverage of 0.07 ML (spectrum f). With increasing CHT coverage this 300 K cyclohexane peak increases. At a coverage of 0.15 ML, cyclohexane formation at 240 K begins and increases with increasing coverage (spectra f–a, Figure 3). Increases in low-temperature (260 K) benzene

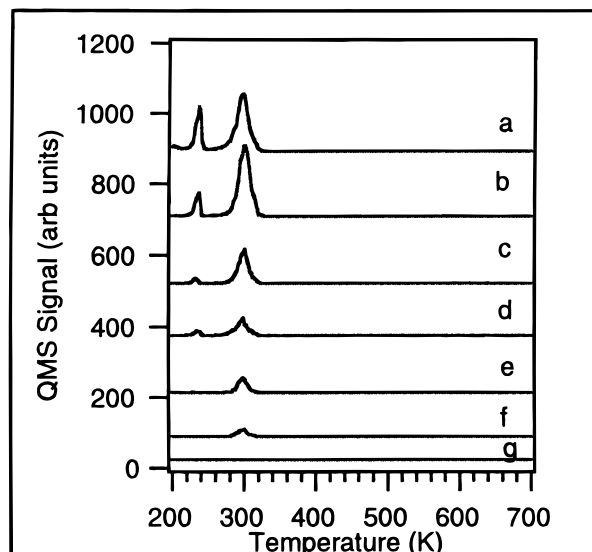


Figure 3. Cyclohexane desorption from varying exposures of CHT. Coverages are as follows: (a) 0.27, (b) 0.25, (c) 0.20, (d) 0.15, (e) 0.10, (f) 0.07, and (g) 0.03 ML. The temperature scale has been selected to accentuate cyclohexane features. Higher coverages of CHT yield cyclohexane at 240 K, believed to be the temperature of C–S bond activation. The 300 K peak is from hydrogenation of adsorbed cyclohexyl intermediates.

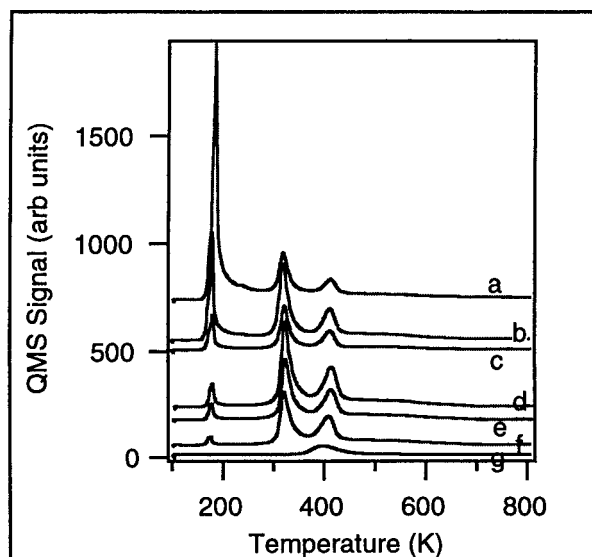


Figure 4. Hydrogen desorption from varying exposures of CHT. Coverages are as follows: (a) 0.27, (b) 0.25, (c) 0.20, (d) 0.15, (e) 0.10, (f) 0.07, and (g) 0.03 ML. The 180 K feature is from molecular desorption of CHT. Free hydrogen desorption (from thiol and hydrocarbon decomposition) occurs at 310 K, with H_2 from dehydrogenation occurs above 400 K. At very low exposure (0.002 langmuir), only high-temperature hydrogen is observed, associated with nonselective decomposition.

desorption have been observed immediately following C–S bond scission in benzenethiol on the Ni(111) surface as exposure of the thiol increased. However, low-temperature benzene is present even at low benzenethiol coverages. This suggests a stronger interaction of the cyclohexyl fragment with the surface compared to phenyl fragments from benzenethiol. The yield of cyclohexene, cyclohexadiene, and benzene, the other organic products, also increases with increasing concentration of CHT.

The hydrogen peaks observed following CHT adsorption clearly indicate that multiple processes are occurring (Figure 4). For the lowest coverage (0.03 ML), a single broad hydrogen peak is observed between 350 and 450 K (spectrum g, Figure

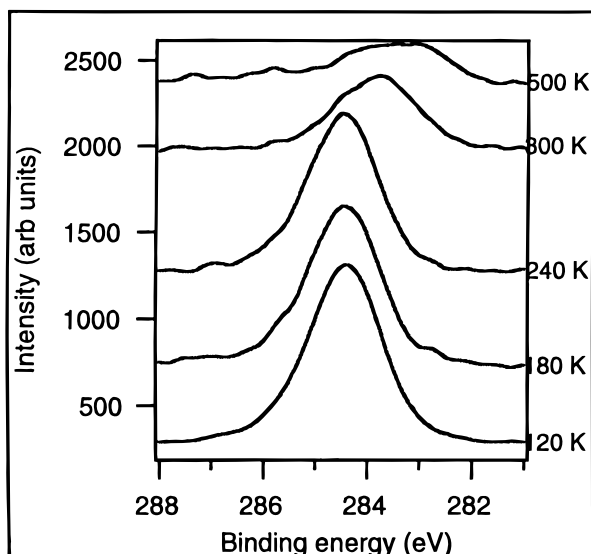


Figure 5. Carbon 1s XPS spectra of 0.25 ML of CHT on Ni(111), annealed from 120 to 500 K. The shift in C 1s binding energy at 300 K is due to increases C–Ni bonding following surface reaction.

4). The absence of a free hydrogen peak in this case suggests that thiolate is not being formed for these low coverages. No other desorbing products are observed. For coverages above 0.07 ML free hydrogen desorption in the 300–310 K range is observed in addition to a high-temperature hydrogen peak in the 380–450 K range with a shoulder extending to 600 K (spectra f–a). The free hydrogen originates from the dissociation of the thiol, while high-temperature hydrogen is caused by dehydrogenation of hydrocarbon intermediates. The amount of hydrogen desorbing quickly saturates with increasing CHT coverage. The leading edges of the second set of organic products occur in the same temperature range as free hydrogen desorption.

Even for small CHT coverages, significant CHT molecular desorption is observed at 180 K. Fragmentation of this molecular desorption is responsible for the peaks at 180 K for all the masses discussed above (Figures 2 and 4). There is no evidence for the formation of any other products at this temperature. This unexpected molecular desorption indicates that a weakly adsorbed form of CHT is present even for submonolayer coverages. Significant thiolate formation does not occur for low coverages as indicated by the absence of free hydrogen for an initial coverage of 0.03 ML. Multiple deuterium incorporation is also observed for CHT which desorbs at 180 K, clearly indicating that the cyclohexyl ring must be involved in bonding to the surface for this weakly adsorbed form. TPD experiments show that cyclohexane desorbs from a partially sulfided Ni(111) surface in this same temperature range. Taken together, these data suggest that the low-temperature form of cyclohexanethiol is bound to the surface through the ring. Apparently, bonding with the cyclohexyl ring limits conversion to the more stable thiolate form.

The carbon XPS spectra for 0.25 ML of saturated CHT monolayer show that approximately half of the surface carbon is removed as gas-phase products (Figure 5). A saturated monolayer is obtained by annealing the sample to 180 K. The carbon 1s position at 284.5 eV is consistent an adsorbed thiolate.^{17,28} The carbon peak area does not change significantly after annealing the 180 K monolayer to 240 K. This is consistent with the very small cyclohexane TPD peak at 240 K. Most all of the surface intermediates remain adsorbed at 240 K instead of being hydrogenated and desorbing. After the

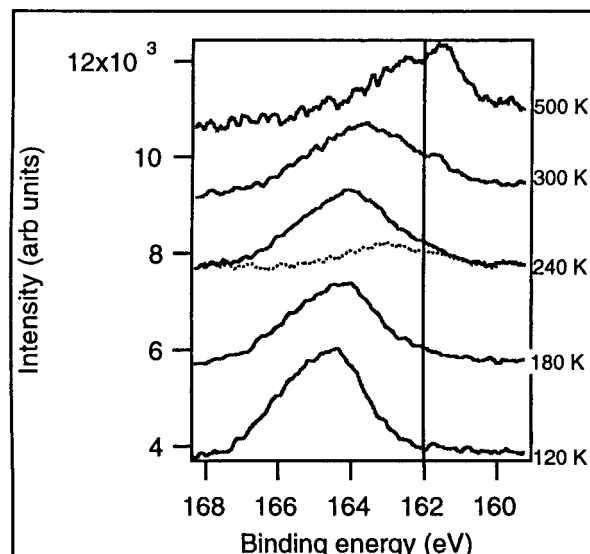


Figure 6. Sulfur 2p XPS spectra of 0.25 ML of CHT on Ni(111), annealed from 120 to 500 K. The dashed line in the 240 K spectra represents the fraction of "inorganic" sulfur bound directly to nickel following C–S bond activation. The solid vertical line indicates the binding energy for inorganic sulfur on the Ni(111) surface.

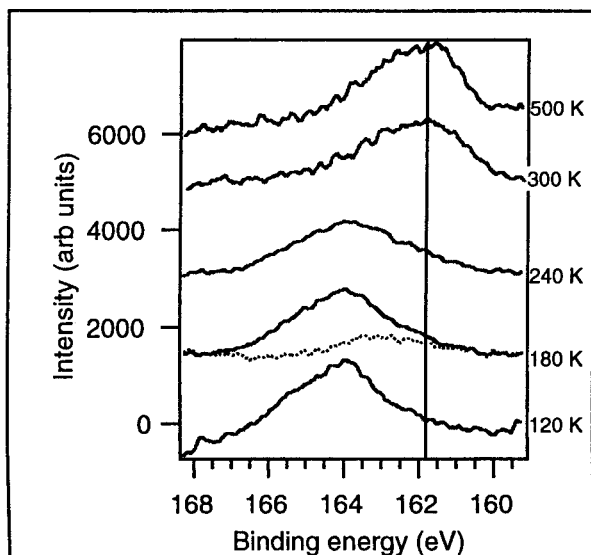
300 K anneal, the amount of carbon on the surface decreases by 50%, indicating that approximately half of the original CHT forms gas-phase products that desorb. TPD indicates that cyclohexane, cyclohexene, cyclohexadiene, and benzene desorb in this temperature range. After annealing to 300 K, the carbon binding energy decreases to 283.7 eV. This decreased binding energy indicates that C–Ni bonding has increased substantially. This result is consistent with the dehydrogenated gas-phase products observed at 300 K and the desorption of free hydrogen. As the temperature continues to increase, the surface carbon content is slightly reduced through desorption of benzene in the 400 K range. Above 500 K surface carbon dissolves into the bulk, and the surface carbon concentration decreases markedly.

High-temperature hydrogen desorption provides an independent confirmation of the yield of desulfurized hydrocarbon formation. A comparison of the amount of hydrogen that desorbs from a saturated hydrogen monolayer (see for example Figure 2) with the amount of reaction limited hydrogen above 350 K from the dehydrogenation of surface intermediates was obtained. An estimate of the yield of desulfurized hydrocarbon can be based on the observation that all hydrogen desorbing above 350 K comes from the dehydrogenation of hydrocarbon intermediates which remain adsorbed. This estimate confirms that approximately half of the original CHT monolayer remains on the surface above 350 K.

The sulfur 2p XPS peak shows that approximately 20% of the C–S bonds are broken at 240 K for a saturated monolayer of CHT (Figure 6). The S 2p peak position (164.4 eV) observed in the 120 K spectrum is consistent with the binding energy for multilayer organic thiol.¹⁷ The S 2p peak decreases to 164.0 eV after annealing to 180 K as expected for a 0.25 ML sulfur bound thiolate on Ni.²⁹ After annealing to 240 K, a shoulder begins to form at 162.0 eV on the sulfur peak, indicating the formation of "inorganic" sulfur bound directly to the metal surface. The dashed line in Figure 6 indicates that approximately 20% of the original thiolate sulfur intensity transformed to inorganic sulfur at 240 K. This XPS result, combined with the 240 K cyclohexane, demonstrates that C–S bond scission begins at 240 K. The temperature for C–S bond

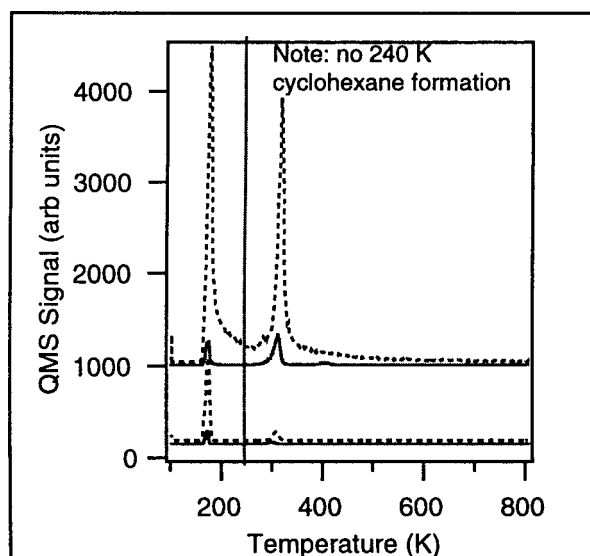
TABLE 1: C–S, C–H, and C–C Bond Strengths in Cyclohexanethiol and Benzenethiol

dissociation energies (kcal/mol)	cyclohexanethiol	benzenethiol
C–S bond	70.5 ^a	86.5 ^b
C–H bond	95.5	111.0
S–H bond	88.5	83.3 ^b

^a Value estimated from ref 31. ^b Reference 31.**Figure 7.** Sulfur 2p XPS spectra of 0.07 ML of CHT on Ni(111), annealed from 120 to 500 K. The dashed line in the 180 K spectra represents the fraction of "inorganic" sulfur bound directly to nickel following low-temperature C–S bond activation. The solid vertical line indicates the binding energy for inorganic sulfur on the Ni(111) surface.

activation in cyclohexanethiol decreases by 20 K relative to the C–S bond activation temperature for benzenethiol.^{10,11} Since the C–S bond strength of 70.5 kcal/mol in CHT is smaller than the 86.5 kcal/mol C–S bond in benzenethiol (Table 1),³¹ C–S bond reactivities correlate with C–S bond strength. Correlation between bond strengths and bond breaking energies suggests that this surface reaction may occur by a radical mechanism as proposed previously in inorganic cluster compounds³² and Co/Mo/S catalysts.³³ After annealing to 300 K, C–S bond activation is more extensive as indicated by the increase in the "inorganic" sulfur at 162.0 eV. The constant size of the overall sulfur peak is consistent with inorganic sulfur remaining on the surface after C–S bond scission. Continued heating above 500 K shows complete conversion to "inorganic" sulfur on the surface, which is the only surface species observed after heating to 800 K.

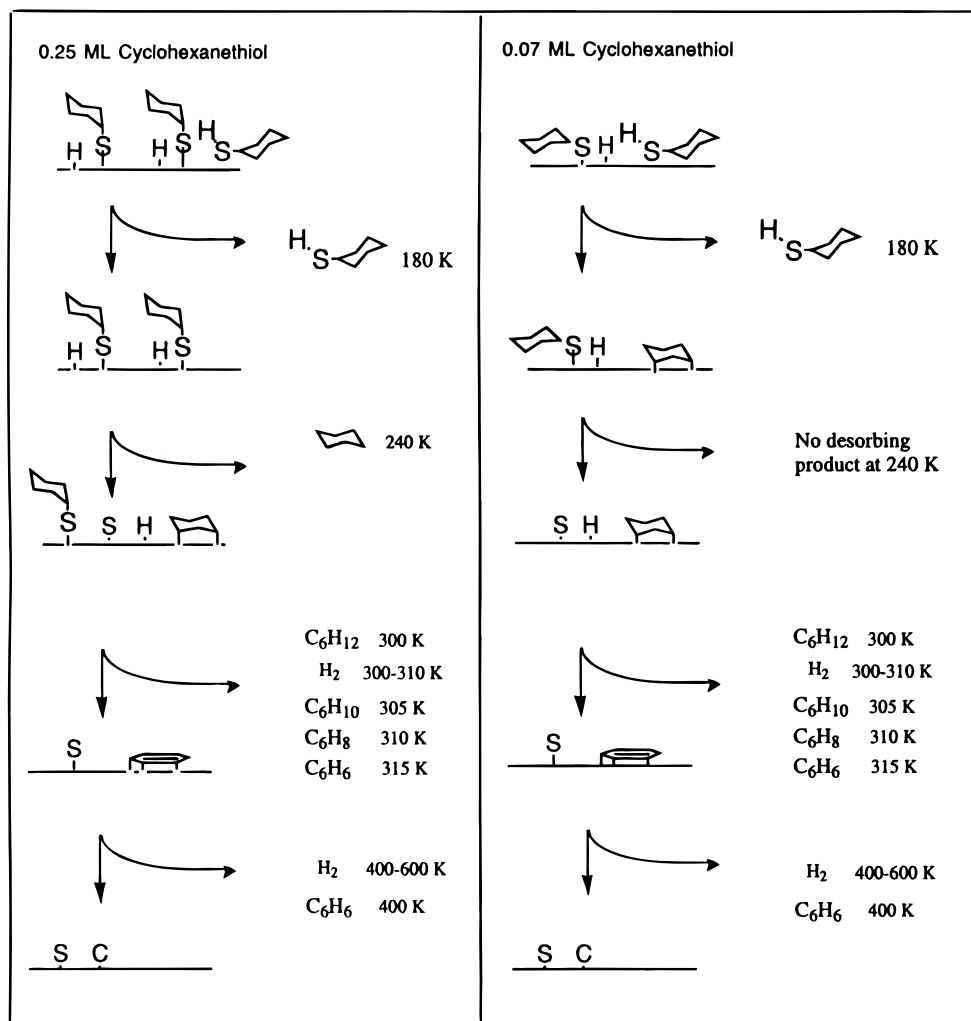
C–S bond activation occurs at lower temperature for low coverages of CHT. Figure 7 presents the sulfur 2p XPS anneal set for an initial coverage of 0.07 ML of CHT on the Ni(111) surface. For both the initial exposure and the 180 K annealed surface, the primary sulfur peak occurs at 164.0 eV. However, significant increased C–S bond breaking is clearly indicated by the appearance of the "inorganic" sulfur peak following the 180 K anneal. Clearly C–S bond scission has already begun at 180 K, even though gas-phase desulfurized products are not observed until 300 K. The dashed line in the 180 K spectrum highlights that approximately 30% of the original submonolayer coverage of CHT appears at a binding energy of 162.1 eV. Increased temperature leads to further formation of inorganic sulfur, since the 164 eV shoulder increases with increasing temperature. By 300 K, all of the submonolayer thiol has undergone C–S bond scission to produce inorganic sulfur.

**Figure 8.** Primary products for the reaction of 0.07 ML of CHT on Ni(111), both from the clean surface (solid lines) and in the presence of 10 langmuirs of preadsorbed H₂ (dashed lines). The upper curves represent benzene desorption, and the lower curves are cyclohexane. Additional hydrogen is shown to greatly increase both the molecular desorption (180 K peak) and both of the products.

Coadsorbed surface hydrogen does not affect reactivity for a saturated monolayer of cyclohexanethiol on the Ni(111) surface. The comparison of cyclohexane formation with and without hydrogen (data not shown) indicates that hydrogen does not play a significant role in the activation of the C–S bond. No change is observed in either the temperature or yield of the 240 K cyclohexane peak. If the C–S bond breaking mechanism involved surface hydrogen, either an increased yield or temperature decrease would be anticipated with increased surface hydrogen. Hydrogen is not involved in breaking the C–S bond in benzenethiol on the Ni(111); rather, direct interaction with the metal is the primary C–S bond activation mechanism,¹¹ as discussed in the Introduction. A slight decrease in yield is observed in all the organic gas-phase products with increasing hydrogen, which correlates with a slight decrease in thiol uptake caused by preadsorbed hydrogen (confirmed by AES). Aside from the slight reduction in the amount of desorbing benzene, the only large change is an increase in the temperature of benzene formation at 400 K in the presence of hydrogen. A similar increase was observed from high-temperature benzene formation from benzenethiol on Ni(111) and was attributed to an increase in the stability of the associated intermediate.¹¹ The similarity of the responses to coadsorbed hydrogen suggests that similar dehydrogenated cyclic intermediates are formed in both cases.

Hydrogen preexposure increases the yield of high-temperature gas-phase products for submonolayer coverages of CHT on the Ni(111) surface. Figure 8 shows that a larger yield of organic products is observed from the reaction of 0.07 ML of CHT with 10 langmuirs of predosed H₂ (dashed) compared to the yield from a clean surface (solid). This increase in yield is consistent with a stabilization of surface intermediates by preadsorbed hydrogen. No cyclohexane formation is observed at 240 K at this coverage, even in the presence of coadsorbed hydrogen. This fact, coupled to the behavior of the 240 K peak with increasing CHT coverages (Figure 3), suggests that formation of gas-phase cyclohexane is favored only for large CHT coverage. The 240 K peak occurs when surface crowding is sufficient to decrease ring/surface interactions, facilitating the desorption of cyclohexane.

**Reaction pathway diagram for adsorbed cyclohexanethiol
(0.25 ML, and 0.07 ML coverages)**



similar reactions are observed at low and high coverage. CHT adsorbs at 120 K on the Ni(111) surface primarily as cyclohexylthiolate, producing a stoichiometric amount of surface hydrogen. In contrast to other simple thiols such as benzenethiol, however, the cyclohexyl ring interacts with the surface, as shown by deuterium incorporation. In addition, a small amount of CHT remains molecular following adsorption at low temperature, producing a molecular CHT peak at 180 K even at low coverages. C–S bond scission in the thiolate was observed at 240 K as evidenced both by sulfur XPS and by a small amount of cyclohexane desorption during TPD experiments. This C–S bond-breaking temperature is 20 K lower than the C–S bond-breaking temperature for benzenethiol on the Ni(111) surface. This direct correlation between C–S reactivities and C–S bond strengths suggests a radical mechanism. The small yield of cyclohexane at this temperature is attributed to extensive interaction between the cyclohexyl group and the surface as demonstrated by deuterium incorporation and the dependence of the 240 K peak on CHT concentration. Low C–H bond strength in CHT and steric factors explain this result. The majority of the resulting desulfurized intermediates remain on the surface until 300 K, where cyclohexane, cyclohexene, cyclohexadiene, and benzene desorption begins. Disproportionation of any remaining hydrocarbons leads to a final benzene peak at 400 K and complete dehydrogenation, leaving only surface sulfur and absorbed carbon. C–S bond scission for low coverages of cyclohexanethiol occurs as low as 180 K, but nonselective decomposition dominates. Hydrogen preadsorption for the low coverages of CHT increases the yield of desorbing organic products without altering desorption temperatures. However, hydrogen preadsorption does not significantly affect the C–S bond activation temperature for CHT, indicating that the C–S bond-breaking mechanism is independent of surface hydrogen. Taken together, these data indicate that the mechanism for C–S bond activation is the same for cyclohexanethiol and benzenethiol. The dominant mechanism does not involve hydrogen but instead involves direct interaction between the C–S bond and the metal surface for all coverages of cyclohexanethiol.

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