

Model Hydrodesulfurization Reactions: Saturated C₄S Molecules on Mo(110)

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Abstract: The reactions of tetrahydrothiophene and 1-butanethiol on Mo(110) have been investigated by using temperature-programmed reaction spectroscopy, isotopic exchange reactions, and Auger electron spectroscopy. At low exposures, tetrahydrothiophene decomposes below 400 K to gaseous dihydrogen and surface carbon and sulfur. Higher tetrahydrothiophene exposures also result in reaction limited formation of butane and butene at 350 and 380 K, respectively. Preadsorption of a saturation coverage of hydrogen or deuterium atoms decreases the temperature at which butane is formed by 50 K and increases the yield of butane by a factor of approximately 6 at reaction saturation. The butene formation peak is unaffected by the presence of excess surface hydrogen. Reversible desorption of molecularly bound tetrahydrothiophene from the Mo(110) surface is observed at 310 K. In the absence of preadsorbed hydrogen, approximately 25% of the tetrahydrothiophene that reacts forms hydrocarbons, as measured by Auger electron spectroscopy. An irreversibly bound hydrocarbon fragment is present on the surface which decomposes at 565 K to produce gaseous dihydrogen. The butane, butene, and dihydrogen incorporate surface deuterium. The proposed mechanism for this reaction is initial hydrogenation of one of the α -carbon atoms with accompanying C-S bond scission. Hydrogenation of the resulting intermediate at the α -carbon yields butane. Alternatively, elimination of a hydrogen atom bonded to a carbon located β to sulfur in the partially hydrogenated intermediate results in 1-butene formation. The reaction of 1-butanethiol was investigated to test the mechanism since 1-butanethiol will yield the intermediate proposed for tetrahydrothiophene reaction if S-H bond scission is the first step in the reaction of 1-butanethiol. The reaction of 1-butanethiol is, in fact, analogous to the reaction of tetrahydrothiophene. Molecular hydrogen, butane, and butene are produced in the same temperature regime as for the tetrahydrothiophene reaction on Mo(110), with butane and butene formation occurring at 305 and 355 K, respectively. There is an order of magnitude greater hydrocarbon yield from reaction of 1-butanethiol, compared to tetrahydrothiophene. At most one surface deuterium atom is incorporated into the butane produced during 1-butanethiol decomposition, while no surface deuterium is incorporated into the butene produced. These results further support the proposed mechanism.

Hydrodesulfurization, the catalytic removal of sulfur from sulfur-containing molecules in petroleum feedstocks, is a process of considerable industrial importance.¹ Hydrodesulfurization reactions are performed industrially with supported molybdenum based catalysts. A MoS₂-like phase is generally considered to be the catalytically active material.² The mechanistic details of the hydrodesulfurization reaction are not well understood. For instance, it is not known whether the first step of thiophene hydrodesulfurization involves hydrogenation of the aromatic ring or scission of a C-S bond.³

The reactions of simple sulfur-containing hydrocarbons on single-crystal transition-metal surfaces under ultra-high vacuum might be useful models for hydrodesulfurization. This investigation concerns the adsorption and reactions of saturated C₄S compounds on the Mo(110) surface under ultra-high vacuum. The cyclic molecule tetrahydrothiophene (C₄H₈S) was studied because of its close structural relationship to thiophene, which is a prototypical substrate for the hydrodesulfurization process. Thiophene itself decomposes to surface carbon, surface sulfur, and gaseous hydrogen during temperature-programmed reaction on Mo(110). Its reactions will be described elsewhere.⁴ In contrast to thiophene, the fully hydrogenated C₄S heterocycle tetrahydrothiophene decomposes on Mo(110) to yield butane and butene, as well as dihydrogen and surface carbon and sulfur, during temperature-programmed reaction.

The relative temperatures for butane and butene formation from tetrahydrothiophene on Mo(110) and the relationship between the hydrocarbon and dihydrogen formation features suggest a mechanism in which tetrahydrothiophene is hydrogenated at the carbon atom located α to sulfur, forming a straight chain butyl

thiolate intermediate. Depending on the surface hydrogen concentration, the adsorbed butyl thiolate may then undergo hydrogenation or dehydrogenation to produce butane or butene, respectively. The reaction of the straight chain thiol, 1-butanethiol (C₄H₉SH), was investigated to test the proposed mechanism, given that it is expected to readily yield a surface butyl thiolate. In fact, 1-butanethiol yields the same products with energetics similar to tetrahydrothiophene but with a hydrocarbon product yield greater by approximately an order of magnitude.

The surface chemistry of tetrahydrothiophene has not been extensively studied. Ultraviolet photoemission studies of tetrahydrothiophene on Cu(110) have been published which are consistent with molecular adsorption of tetrahydrothiophene as a Lewis base.⁵ A previous investigation of tetrahydrothiophene on W(211) reported reactivity similar to the Mo(110) surface, with butane and butene formation observed at high tetrahydrothiophene exposures.⁶ Reactions of tetrahydrothiophene over sulfided Co-molybdate catalysts supported on alumina have been reported in which hydrodeacyclization to form 1-butanethiol was the primary process.^{3a} Later reports of tetrahydrothiophene reactions on a supported Co-Mo catalyst reported primarily desulfurization resulting in butane, 1- and 2-butene, and 1,3-butadiene.^{3b} Furthermore, thiophene, tetrahydrothiophene and 1-butanethiol all formed the same products, although with different distributions: 1-butanethiol yielded significantly higher proportions of butane compared to the cyclic molecules.^{3b} The high surface area reactions were interpreted in terms of a mechanism in which hydrogenation of the α -carbon preceded C-S bond scission. The surface chemistry of 1-butanethiol on single-crystal surfaces has not to our knowledge been reported. Neff and Kitching have investigated the reactions of 1-butanethiol on evaporated nickel films.⁷ Several groups have studied the adsorption and reactions

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of the closely related molecule, methanethiol, on Pt(111),⁸ W(211),⁹ and Cu(100).¹⁰

Experimental Section

All experiments were performed in an ultra-high vacuum chamber with a working base pressure of approximately 2×10^{-10} Torr. The chamber was continuously pumped with a 110 L/s ion getter pump (Varian) and a cryopump (CTI Cryogenics). The chamber was intermittently pumped by a titanium sublimation pump (Varian). The vacuum system was equipped with electron optics for retarding field Auger electron spectroscopy and low energy electron diffraction (Varian). The Mo(110) crystal was mounted on a sample manipulator capable of rotation and x , y , and z translation. The sample was in thermal contact with a liquid nitrogen cooled reservoir. The sample cooled from room temperature to 130 K, the approximate temperature of adsorption unless otherwise stated, in 5 min. The sample was heated with either radiative or electron bombardment heating. Radiative heating was performed by resistively heating a tungsten filament positioned approximately 0.06 in. behind the molybdenum crystal. Radiative heating rates were approximately constant with a small linear decrease in rate as the crystal heated, with $dT/dt = 16 \pm 1$ K/s in the range of 120–700 K. During electron bombardment heating, the crystal was positively biased with respect to the grounded filament at 500 V. The crystal could be heated at 2500 K with electron bombardment heating. All temperature-programmed reaction data were obtained with radiative heating. Electron bombardment heating was used in sample cleaning, described below. The sample temperature was measured by a W-5% Re/W-26% Re thermocouple junction spotwelded to the upper edge of the molybdenum crystal.

The Mo(110) crystal, obtained from Metal Crystals, Ltd., was oriented to within 0.5° of the (110) plane with Laue X-ray back diffraction. A wafer approximately 0.10 in. thick was cut from the crystal rod by spark erosion. After cutting, the Mo(110) crystal was ground, reoriented, and etched. The etch was a room temperature solution of potassium hydroxide (10 g) and potassium ferricyanide (10 g) in distilled water (to make 200 mL of solution).¹¹ Mechanical polishing of the oriented Mo(110) wafer was carried out in successive steps. The initial polishing steps were with 400, 600, and 800 grit SiC powder suspended in water. Final polishing was carried out successively with 6 and 1 μm diamond paste. The orientation and quality of the polished molybdenum crystal were checked with Laue X-ray back diffraction and low-energy electron diffraction (LEED) before and after placement in the vacuum system, respectively. Both faces of the crystal wafer were oriented and polished.

Dosing of all reagents onto the molybdenum surface was performed with directed dosers, similar to those described elsewhere.¹² Exposures are given in units of Torr-s. A Torr-s is defined as the product of the dosing time and the pressure maintained in the reservoir behind the flow constriction tube. Exposures are referenced to reaction saturation, defined as the dose at which growth of multilayers of the adsorbate is first observed and no further reaction proceeds. The backing pressure was the same for a given molecule in all experiments. Thus, the only variable is the time of dose. Under these conditions the dose is linearly related to the coverage, assuming a constant sticking probability as a function of coverage. This is a reasonable assumption given that both tetrahydrothiophene and 1-butanethiol form multilayers under dosing conditions, suggesting that the adsorption probability is approximately one. The gas manifold was filled with reagent immediately before each experiment in order to minimize decomposition in the stainless steel lines. Sample purity was checked by dosing the reagent into the vacuum system after an experiment and monitoring the gas composition mass spectrometrically.

Tetrahydrothiophene (99.0% purity) and 1-butanethiol (99.0% purity) were obtained from Aldrich Chemicals. Both were dried over sodium sulfate. After being dried, tetrahydrothiophene was vacuum distilled, and 1-butanethiol was distilled under dry nitrogen. The purity of both tetrahydrothiophene and 1-butanethiol were checked with mass spectrometry and ¹H NMR spectroscopy and determined to be of high purity. All liquids were degassed by freeze-pump-thaw cycles prior to use each day. The following gaseous reagents were obtained from Matheson and used without further purification: hydrogen (98.0% purity), deuterium (99.0% purity), and oxygen (99.8% purity).

The crystal was cleaned by cycles of heating for 4 to 10 min at 1200 K in a background pressure of 1×10^{-7} Torr of dioxygen and then

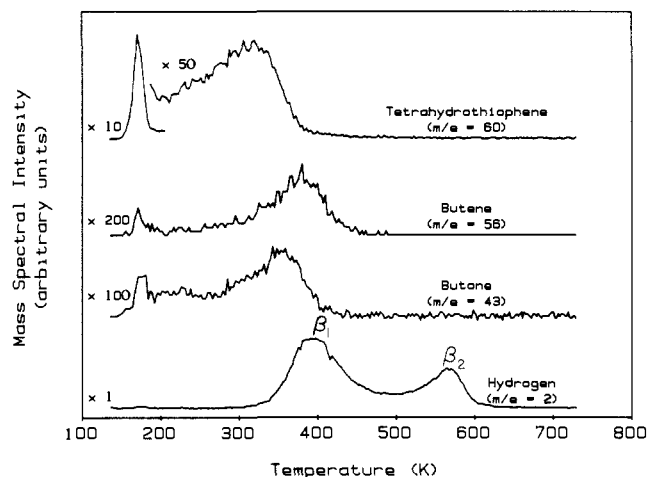


Figure 1. Temperature-programmed reaction spectra of tetrahydrothiophene on Mo(110). The multiplication factors are referenced to hydrogen and are uncorrected for degree of fragmentation and ionization efficiency in the mass spectrometer. The sharp peak in the m/e 60 spectrum at 170 K is due to sublimation of tetrahydrothiophene multilayers, indicating that the reaction is saturated. The masses shown are the most intense observed for which only one peak contributed to the signal.

Table I. Relative Ion Yields for the Seven Most Intense Ions for Molecules Investigated in the Work^{a,b}

molecule	mass/charge (% yield)						
	27	60	45	46	39	47	27
tetrahydrothiophene	27 (100)	60 (86)	45 (71)	46 (58)	39 (48)	47 (42)	27 (37)
1-butanethiol	41 (100)	27 (89)	29 (72)	56 (46)	39 (40)	27 (30)	47 (26)
butane	43 (100)	29 (70)	28 (70)	27 (70)	41 (43)	39 (21)	42 (19)
1-butene	41 (100)	28 (60)	27 (56)	39 (52)	29 (51)	26 (23)	56 (19)
trans-butene	41 (100)	28 (56)	27 (56)	39 (48)	29 (31)	56 (25)	26 (21)

^a Measured by using the experimental configuration described herein. ^b The molecular ions of tetrahydrothiophene (m/e 88), 1-butanethiol (m/e 90), and butane (m/e 58) are less than 10% as intense as the most intense ion in their respective mass spectra.

flashing in vacuum to 1900 K. Crystal cleanliness and order were determined with retarding field Auger electron spectroscopy and LEED, respectively.

Temperature-programmed reaction data were collected with a quadrupole mass spectrometer (UTI-100C) interfaced to an IBM personal computer. All data reported were obtained by collecting intensity-temperature profiles for up to eight masses in a given experiment. Another program allowing for data collection of up to 100 masses in a given experiment¹³ was used to check for unanticipated products, assuring that the reported products were the only ones formed. The quadrupole mass spectrometer was enclosed in a double jacketed shield equipped with a flag which could be rotated to vary the entrance aperture. The internal jacket was cooled with liquid nitrogen during all temperature-programmed reaction experiments. Before data collection the flag was rotated so that the entrance aperture to the mass spectrometer was 0.0625 in. The crystal was positioned 0.125 in. from the aperture. This configuration optimized detection of molecules desorbing normal to and from the center of the crystal surface, and it minimized the contribution of background reaction and/or desorption to the spectra. The aperture was opened to 2.5 in. to analyze the background or dose gases.

Results

Tetrahydrothiophene. Temperature-programmed reaction data obtained subsequent to adsorption of multilayers of tetrahydrothiophene on Mo(110) are presented in Figure 1. The volatile

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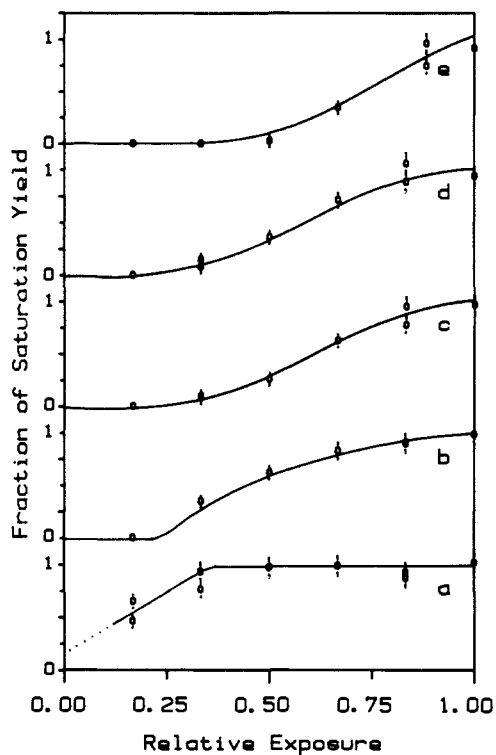


Figure 2. Fractional temperature-programmed reaction yield of (a) β_1 -hydrogen, (b) β_2 -hydrogen, (c) butane, (d) butene, and (e) tetrahydrothiophene vs. tetrahydrothiophene exposure. The product yields are referenced to their respective saturation values. An exposure of 1.00 corresponds to reaction saturation and the onset of multilayer desorption. The error bars are $\pm 10\%$ of the integrated signal, the maximum variation observed between identical experiments. The nonzero y intercept of the β_1 -H₂ curve is due to the adsorption of background hydrogen by the crystal.

products are dihydrogen in two peaks labeled β_1 and β_2 (shown as m/e 2), butane (m/e 43), butene (m/e 56), and tetrahydrothiophene (m/e 60). The masses presented in Figure 1 are the most intense observed for which only one peak contributed to the signal. The relative yields of the seven most intense ions of tetrahydrothiophene, butane, 1-butene, and *trans*-butene measured in our experimental configuration are listed in Table I. Temperature-programmed reaction spectra have been recorded for all masses listed in Table I. Within experimental error, the relative ion yields of the peaks assigned as butane, butene, and tetrahydrothiophene agree with the ion yields shown in Table I. As Table I demonstrates, the specific isomer(s) of butene produced cannot be determined on the basis of the mass spectral data due to the fact that all butene isomers have similar fragmentation patterns.¹⁴ Furthermore, the fragmentation pattern depends on the temperature of the analyzed gas,¹⁵ precluding determination of the butene isomer(s).

Figure 2 depicts the integrated peak intensities of the four products detected, normalized to their saturation values, as a function of tetrahydrothiophene exposure. The hydrogen:butane:butene:tetrahydrothiophene ratio at saturation is approximately 100:1:1:4.¹⁶ Although this estimate is rather crude, the ratio demonstrates that well under half of the tetrahydrothiophene

decomposes to yield hydrocarbon products.

Temperature-programmed reaction of low exposures (2.5 Torr-s = 0.17 saturation) of tetrahydrothiophene adsorbed on Mo(110) results exclusively in irreversible decomposition, producing molecular hydrogen in two poorly resolved peaks at 400 and 420 K, surface carbon, and surface sulfur. The 400 and 420 K H₂ features, referred to hereafter as β_1 , coalesce and increase in intensity up to tetrahydrothiophene exposures of 7.5 Torr-s, which correspond to approximately 0.50 of the saturation exposure. The temperature maximum of the β_1 -H₂ peak at saturation is 390 K. Hydrogen adsorbed to high coverage on clean Mo(110) desorbs in a broad peak at 420 K,¹⁷ so the β_1 peak may be desorption or reaction limited. The nature of the β_1 peak will be further discussed below. An additional reaction limited molecular hydrogen peak appears at 565 K for tetrahydrothiophene exposures greater than 5 Torr-s = 0.33 saturation. The 565 K H₂ peak, labeled β_2 , increases in intensity with increasing exposure, saturating at a tetrahydrothiophene dose of 15 Torr-s = 1.0 saturation. If the Mo(110) surface is saturated with tetrahydrothiophene, heated to 475 K (the saddle point between the β_1 and β_2 peaks), and cooled to 135 K, then only β_2 -hydrogen is detected in a temperature-programmed reaction experiment. Thus, there is no exchange between the β_1 and β_2 sites after all β_1 -H₂ has left the surface. The β_2 -H₂ is proposed to originate from the decomposition of an irreversibly bound hydrogen bearing fragment.

The butane and butene peaks first appear at tetrahydrothiophene exposures of 5 Torr-s = 0.33 saturation, the lowest exposure that results in formation of β_2 -dihydrogen. The temperatures of butane and butene formation are slightly different with butane formation peaking at 350 K and butene formation at 380 K. Both peaks are reaction limited. Butane desorbs at 160 K with no or little accompanying decomposition, and 1- and *trans*-2-butene undergo decomposition and reversible molecular desorption below 300 K when adsorbed on Mo(110) at high coverage.⁴ The onset of butane formation precedes by approximately 40 K the rise in the β_1 -hydrogen peak. The leading edge of the butene peak lags 10 K behind the leading edge of the β_1 peak. The amounts of butane and butene formed from tetrahydrothiophene reaction increase together with increasing exposure, saturating at an exposure of 12.5 Torr-s = 0.83 total reaction saturation. Preadsorption of a saturation coverage of atomic hydrogen shifts the butane formation peak 115 K down in temperature to 305 K. In addition, the butane yield is greater by a factor of approximately 6 compared to reaction without hydrogen atom preadsorption. The butene formation peak is unaffected by hydrogen preadsorption. These results are consistent with C-H bond formation being rate limiting in butane production but not in butene formation.

No tetrahydrothiophene desorption is detected at low exposures. Desorption of reversibly bound tetrahydrothiophene commences at exposures of 7.5 Torr-s = 0.50 of the saturation exposure, with trace amounts of desorption at 360 K. As the exposure increases, more tetrahydrothiophene desorbs, and the peak temperature decreases, to 310 K at reaction saturation. At exposures of 15 Torr-s, a sharp tetrahydrothiophene desorption feature centered at 170 K appears in the temperature-programmed reaction spectrum. This sharp peak does not saturate. The peak temperature increases with increasing tetrahydrothiophene exposure, consistent with a zero-order desorption process. This peak is attributed to sublimation of tetrahydrothiophene multilayers. Its appearance corresponds to reaction saturation.

Auger electron spectra, measured after temperature-programmed reaction to 750 K, are used to estimate the fraction of tetrahydrothiophene that decomposes to butane and butene. There was no evidence for electron-stimulated desorption of the carbon and sulfur residue or diffusion of carbon or sulfur into the bulk in these measurements. The Auger spectra measured did not significantly change subsequent to exposure to the electron beam for times similar to those required for Auger data collection (ca. 15 min). In addition, no differences in $R_{C/S}$, the carbon/sulfur

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(16) These ratios were calculated from the integrated peaks corrected for degree of fragmentation, ionization efficiency, and quadrupole transmission efficiency in the mass spectrometer. The correction factors were derived from published sources.¹⁴ Each mass spectrometer has its own set of response characteristics, so this ratio is a crude estimate. Also the liquid nitrogen cryoshield around the mass spectrometer increases the local pumping speed of condensable gases, resulting in an overestimate of the relative hydrogen yield.

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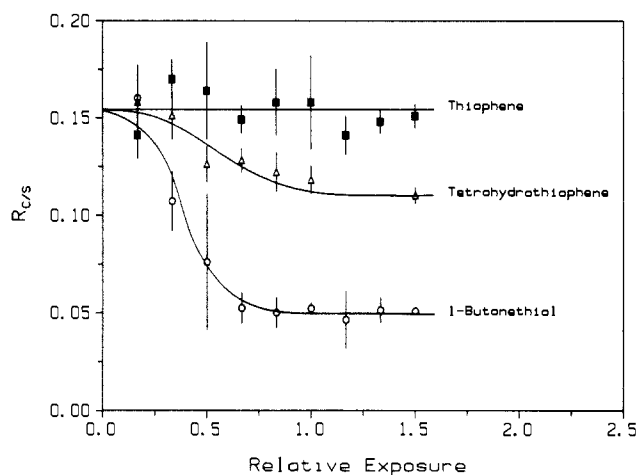


Figure 3. $R_{C/S}$, the C/S Auger ratio, after temperature-programmed reaction vs. adsorbate dose. The adsorbates thiophene, tetrahydrothiophene, and 1-butanethiol are represented by filled squares, triangles, and circles, respectively. An exposure of 1.00 is that required for reaction saturation. The error bars are statistically derived, and each point is the average of at least five experiments.

Auger ratio, were evident when the residue was heated to 1200 K compared to the 750 K anneal. Thus, the Auger ratios are a reliable measure of the amount of carbon and sulfur deposited as a result of tetrahydrothiophene decomposition. Figure 3 plots the ratio, $R_{C/S}$, of the peak-to-peak heights of the derivative spectrum of the C(KLL) transitions at 272 eV to the sum of the peak heights of the Mo(MNN) and S(LMM) Auger transitions at 148 and 152 eV, respectively, vs. the relative tetrahydrothiophene dose. The Mo(MNN) and S(LMM) derivative intensities were added because they overlap in energy and are impossible to deconvolute. At tetrahydrothiophene exposures of 2.5 Torr-s = 0.17 saturation, $R_{C/S} = 0.16 \pm 0.01$. This ratio is in good correspondence with the $R_{C/S}$ ratio determined for thiophene, where $R_{C/S} = 0.15 \pm 0.01$ at all exposures (Figure 3). Thiophene does not yield any hydrocarbon products, but it decomposes to surface carbon and sulfur and gaseous dihydrogen on Mo(110).⁴ Thus, the C/S Auger ratio measured following thiophene decomposition references a C_4S surface stoichiometry. The equivalence of the $R_{C/S}$ values within experimental error for thiophene and tetrahydrothiophene at low exposures confirms that no hydrocarbon formation occurs in this tetrahydrothiophene coverage regime. Increasing tetrahydrothiophene exposures result in a decrease of $R_{C/S}$, indicating the loss of surface carbon via hydrocarbon formation. The experimentally determined value of $R_{C/S}$ at reaction saturation is 0.12 ± 0.01 . Comparison of this value with the low-exposure limit allows a rough estimate of the fractional hydrocarbon yield. Approximately 25% of the tetrahydrothiophene that decomposes forms hydrocarbons at reaction saturation. The Auger electron spectroscopy derived hydrocarbon yield is in reasonable agreement with the estimated amount of hydrocarbon formation derived from the relative ionization efficiencies and fragmentation patterns of tetrahydrothiophene, butene, and butane (see above) and is considered a more reliable measure of the hydrocarbon yield due to the large number of assumptions made in calculating the hydrocarbon yields from the mass spectral data.¹⁵

Deuterium preadsorption experiments were performed to probe for H-D exchange processes in reversibly adsorbed tetrahydrothiophene and in the surface intermediate(s) that yield butane, butene, and dihydrogen. In these experiments, a saturation dose of deuterium (120 Torr-s) was preadsorbed as the Mo(110) crystal cooled from room temperature. After cooling to 135 K, tetrahydrothiophene was adsorbed at an exposure greater than that required for reaction saturation. The tetrahydrothiophene desorption peak broadens if surface deuterium is present, but no deuterium incorporation into the reversibly bound tetrahydrothiophene is observed. Thus, no H-D exchange occurs in reversibly bound tetrahydrothiophene.

Table II. Integrated Peak Areas of the β_1 - and β_2 -H₂ Peaks for All Isotopic Combinations: Reaction of Adsorbed D + Tetrahydrothiophene at Saturation^a

isotopic combination	β_1	β_2
H ₂	1.0	0.18
HD	2.8	0.27
D ₂	1.4	0.05

^a The values are normalized to the β_1 -H₂ peak and are uncorrected for relative ionization efficiencies in the mass spectrometer.

All three possible hydrogen/deuterium isotopic combinations are observed in the β_1 - and β_2 -dihydrogen formation peaks. The relative integrated intensities of the H₂, HD, and D₂ produced in the β_1 and β_2 temperature regimes are presented in Table II. The β_1 H/D ratio is 0.9. The β_1 -H₂, -HD, and -D₂ peak temperatures are 410, 400, and 390 K, respectively. The β_1 -H₂ and -D₂ peaks are narrower when deuterium is preadsorbed than is the β_1 -H₂ peak when just tetrahydrothiophene is adsorbed, but the β_1 -HD peak is nearly as wide as the β_1 -H₂ peak when only tetrahydrothiophene is adsorbed. The β_1 -H₂ full-width at half-maximum (fwhm) is 70 K when deuterium is not preadsorbed. If deuterium is preadsorbed, the β_1 -H₂ fwhm is 40 K and the β_1 -D₂ fwhm is 50 K. The leading edges of the low-temperature β_1 -HD and -D₂ peaks match and are lower in temperature than the leading edge of the β_1 -H₂ peak, with the onset of production of β_1 -HD and -D₂ at approximately 310 K and of β_1 -H₂ at 380 K. By contrast, the far edges of the β_1 -HD and -H₂ peaks match and are higher in temperature than the far edge of the β_1 -D₂ peak. Our interpretation of the β_1 -hydrogen peak is that it results from a superposition of reaction and desorption-limited hydrogen states. The leading edge of the peak consists mostly of desorption-limited hydrogen, while the far edge consists mostly of reaction-limited hydrogen. An inverse isotope effect does not adequately explain the results for two reasons. It cannot account for the different fwhm values. Also, there is no pronounced isotope effect for hydrogen and deuterium desorbing from clean Mo(110).

Preadsorbed deuterium suppresses the formation of the β_2 peak. Approximately one-fourth as much β_2 -hydrogen is produced if deuterium is preadsorbed. The β_2 -dihydrogen peak exhibits a kinetic isotope effect, with β_2 -D₂ forming at a higher temperature than β_2 -H₂, as expected for a process where C-H bond breaking is the rate-limiting step. The peak temperatures are 520, 550, and 560 K for β_2 -H₂, -HD, and -D₂, respectively. The β_2 H/D ratio is 1.8, while the β_1 H/D ratio is 0.9. Hence, proportionally less deuterium is incorporated into the β_2 peak. If the surface is saturated with tetrahydrothiophene, heated to 475 K (the saddle point between the β_1 and β_2 peaks), dosed to saturation with deuterium, and cooled to 135 K, then no HD or D₂ appears in the β_2 peak. HD and D₂ appear solely as β_1 -hydrogen. Therefore, deuterium incorporation takes place somewhere along the decomposition pathway, but before formation of the fragment which yields β_2 -hydrogen.

Deuterium incorporation is also observed in both butane and butene. The addition of deuterium is evident in that significant amounts of m/e 44 and 57 coincident with m/e 43 and 56, respectively, are present in the temperature-programmed reaction spectra. Mass 44, $C_3H_6D^+$, is a major ion in the mass spectrum of butane-*d*₁ and -*d*₂, while 57 amu, $C_4H_7D^+$, is the parent ion of butene-*d*₁. Because of low signal levels and overlapping fragmentation patterns the extent of deuterium incorporation into butane and butene cannot be determined. The butane production temperature is lower if deuterium is preadsorbed, but the butene production temperature is unchanged. This is consistent with the hydrogen preadsorption results discussed above.

1-Butanethiol. Temperature-programmed reaction data for multilayers of 1-butanethiol adsorbed on Mo(110) at 135 K are presented in Figure 4. As is the case for tetrahydrothiophene, β_1 - and β_2 -dihydrogen (shown as m/e 2), butane (m/e 43), and butene (m/e 56) are produced from reaction on the surface. Again, the relative ion yields of the peaks assigned as butane and butene agree with the ion yields shown in Table I. In addition,

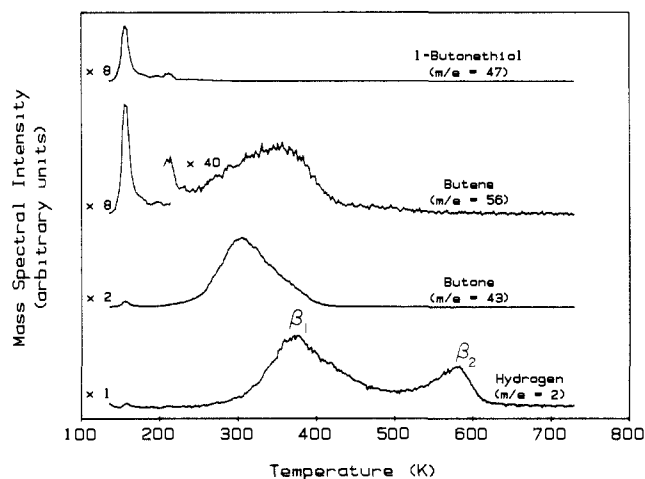


Figure 4. Temperature-programmed reaction spectra of 1-butanethiol on Mo(110). The multiplication factors are referenced to hydrogen and are uncorrected for degree of fragmentation and ionization efficiency in the mass spectrometer. The sharp peaks at 155 K in the m/e 56 and 47 spectra are due to sublimation of 1-butanethiol multilayers, indicating that the reaction is saturated. The peak at 215 K in the m/e 47 spectrum is assigned to di-1-butyl disulfide. The m/e 56 peak at 355 K is due entirely to butene. There is no contribution to this peak from 1-butanethiol, as demonstrated by comparison with the m/e 47 spectrum.

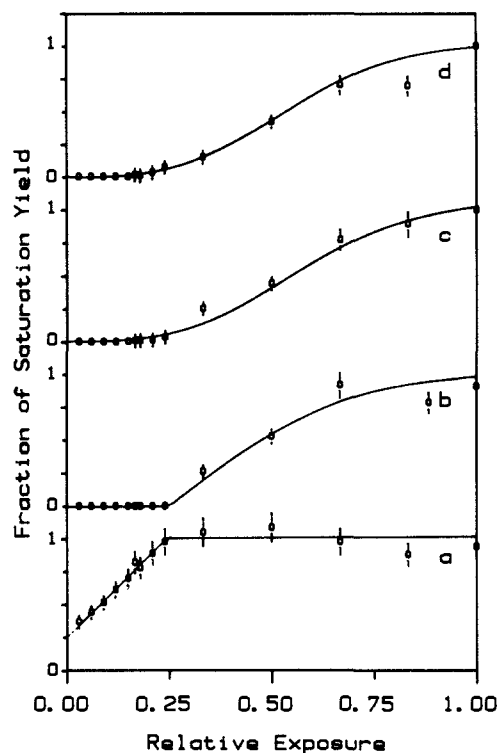


Figure 5. Fractional temperature-programmed reaction yield of (a) β_1 -hydrogen, (b) β_2 -hydrogen, (c) butene, and (d) butene vs. 1-butanethiol exposure. The product yields are referenced to their respective saturation values. An exposure of 1.00 corresponds to reaction saturation and the onset of multilayer desorption. The error bars are $\pm 10\%$ of the integrated signal, the maximum variation observed between experiments. The nonzero y intercept of the β_1 -H₂ curve is due to the adsorption of background hydrogen by the crystal.

formation of a product identified as di-1-butyl disulfide (m/e 47) at 215 K and desorption of 1-butanethiol (m/e 47) at 155 K are observed for multilayer coverages of 1-butanethiol. No other products are detected.

The coverage dependences of the peak areas of β_1 - and β_2 -hydrogen (shown as m/e 2), butane (m/e 43), and butene (m/e 56) formed from 1-butanethiol reaction on Mo(110) are depicted in Figure 5. The hydrogen:butane:butene ratio at saturation,

Table III. Integrated Peak Areas of the β_1 - and β_2 -H₂ Peaks for All Isotopic Combinations: Adsorbed D + 1-Butanethiol at Saturation^a

isotopic combination	β_1	β_2
H ₂	1.00	0.14
HD	3.00	0.26
D ₂	1.84	0.04

^aThe values are normalized to the β_1 -H₂ peak and are uncorrected for relative ionization efficiencies in the mass spectrometer.

calculated from the integrated peaks and corrected for degree of fragmentation and ionization efficiency in the mass spectrometer, is approximately 100:20:5.¹⁶ The total hydrocarbon yield from 1-butanethiol is about ten times the yield from tetrahydrothiophene.

The product identified as di-1-butyl disulfide appears only for multilayer 1-butanethiol exposures. The mass spectrometric fragmentation pattern of 1-butanethiol in the dose matches the fragmentation pattern of the 1-butanethiol multilayers. The fragmentation pattern in the dose does not match the fragmentation pattern of the di-1-butyl disulfide multilayers. This peak is tentatively assigned to a reaction in the multilayer, not an impurity in the 1-butanethiol.

Total decomposition of 1-butanethiol is the only reaction pathway at low exposures (< 5 Torr-s = 0.17 reaction saturation). Hydrogen produced at these exposures is detected as four poorly resolved peaks: at 335, 385, 430, and 485. These peaks are collectively labeled β_1 . The peaks at 335 and 430 K increase rapidly with increasing 1-butanethiol exposure. The four peaks coalesce into one peak at exposures of 10 Torr-s (0.33 reaction saturation). At these exposures the β_1 peak is saturated, and the peak temperature is 380 K. For exposures greater than 10 Torr-s, a reaction-limited molecular β_2 -hydrogen feature appears at 585 K. The β_2 peak saturates at exposures of 30 Torr-s = 1.00 reaction saturation. Exposures of 1-butanethiol greater than 5 Torr-s result in formation of butane and butene at 305 and 355 K, respectively. The hydrocarbon yield increases as a function of 1-butanethiol exposure up to reaction saturation at 30 Torr-s. Preadsorption of hydrogen did not affect either of the hydrocarbon product peaks: the temperature maxima and yield were the same with or without hydrogen preadsorption. This is consistent with a pseudo-first-order reaction for butane formation, attributed to the relatively high coverage of hydrogen in this temperature regime for 1-butanethiol compared to tetrahydrothiophene. This contention is supported by the coincidence of the butane formation peaks from reaction of 1-butanethiol and reaction of a high coverage of hydrogen preadsorbed with tetrahydrothiophene.

Preadsorption of surface deuterium and 1-butanethiol as described above for tetrahydrothiophene results in incorporation of deuterium into all regions of the molecular hydrogen formation spectrum. The results of the deuterium + 1-butanethiol reaction are quantitated in Table III. The β_1 H/D and β_2 H/D ratios from 1-butanethiol are identical within experimental error to the β_1 H/D and β_2 H/D ratios from tetrahydrothiophene. Our interpretation of the H₂, HD, and D₂ data is the same as in the case of tetrahydrothiophene. The lower temperature molecular hydrogen peaks result from a combination of reaction and desorption limited processes, while the 580 K peak is the result of decomposition of an irreversibly bound fragment. The equivalence of the tetrahydrothiophene and 1-butanethiol β_2 H/D ratios suggests that the intermediate(s) which ultimately decompose to β_2 H₂ may in some temperature regime be in equilibrium with surface hydrogen (deuterium).

Deuterium is incorporated into the butane but not into the butene. This is in marked contrast to tetrahydrothiophene, where deuterium is incorporated into both of the hydrocarbons. Because the butane signal levels were much higher during the reaction of 1-butanethiol, the extent of deuterium incorporation into the butane could be measured. Both butane- d_0 (m/e 58) and butane- d_1 (m/e 59) whereas only butane- d_0 (m/e 56) were produced during reaction on the surface. No d_2 or higher deuterated products of either butane or butene were detected. These results

unequivocally demonstrate that butane is formed via a single hydrogenation step with surface H or D while butene formation does not involve hydrogenation. Furthermore, the surface intermediate(s) that react to produce butane and butene do not exchange with surface H or D.

Auger electron spectroscopy is used to estimate the hydrocarbon yield and the relative amount of sulfur deposited on the Mo(110) surface following reaction of 1-butanethiol. $R_{C/S}$ as a function of 1-butanethiol exposure is shown in Figure 3. At exposures below which no hydrocarbon formation is observed, $R_{C/S}$ after 1-butanethiol reaction is 0.16 ± 0.2 , the same within experimental error as $R_{C/S}$ after thiophene reaction (0.15 ± 0.01). This value is representative of the C/S Auger ratio for C_4S stoichiometry on the surface. Increasing 1-butanethiol exposures result in a lower C/S Auger ratio because some of the carbon leaves the surface as hydrocarbons. $R_{C/S}$ at reaction saturation is 0.048 ± 0.005 , or 30% of the ratio measured for C_4S stoichiometry. We therefore estimate that approximately 70% of the surface bound 1-butanethiol reacts to form butane or butene. This is in reasonable agreement with the integrated and corrected temperature-programmed reaction peaks (see above). In addition, the sulfur/molybdenum Auger ratio, $R_{S/Mo}$,¹⁸ is 1.1 ± 0.1 subsequent to reaction of 1-butanethiol adsorbed in multilayer quantities, compared to a ratio of 0.63 ± 0.01 after tetrahydrothiophene reaction at saturation. Thus, approximately twice as much sulfur is deposited by the decomposition of 1-butanethiol. This difference is attributed to the greater packing efficiency of 1-butanethiol and to the fact that no 1-butanethiol desorbs from Mo(110). If tetrahydrothiophene and 1-butanethiol are both assumed to bond to the Mo(110) surface as Lewis bases with a near tetrahedral environment around sulfur, the relative excluded surface area of 1-butanethiol vs. tetrahydrothiophene is approximately 1:1.4.¹⁹ The hydrogen yield from 1-butanethiol is estimated to be approximately six times the yield as that from tetrahydrothiophene reaction on the Mo(110) surface based on the Auger data, the same magnitude estimated from the temperature-programmed reaction data.

Discussion

The striking resemblance of the temperature-programmed reaction spectra of tetrahydrothiophene and 1-butanethiol is strong evidence that they react via a common surface intermediate. The proposed surface intermediate for hydrocarbon formation is an adsorbed butyl thiolate. We propose a reaction mechanism in which both tetrahydrothiophene and 1-butanethiol decompose through the butyl thiolate intermediate (Figure 6). The mechanism accounts for all details of the tetrahydrothiophene and 1-butanethiol reactions.

At low exposures, irreversible and total decomposition of both tetrahydrothiophene and 1-butanethiol is the only reaction pathway, producing surface carbon and sulfur and dihydrogen as the sole volatile product. Dehydrogenation of both molecules must be complete prior to 500 K, based on the molecular hydrogen formation peaks.

At high exposures of either 1-butanethiol or tetrahydrothiophene, not all of the adsorbate decomposes. The presence of molecularly adsorbed tetrahydrothiophene is suggested by its reversible desorption at 310 K. The absence of deuterium incorporation into the desorbed tetrahydrothiophene is strong evidence that the reversibly bound state is wholly associative. Molecularly bound tetrahydrothiophene is proposed to undergo

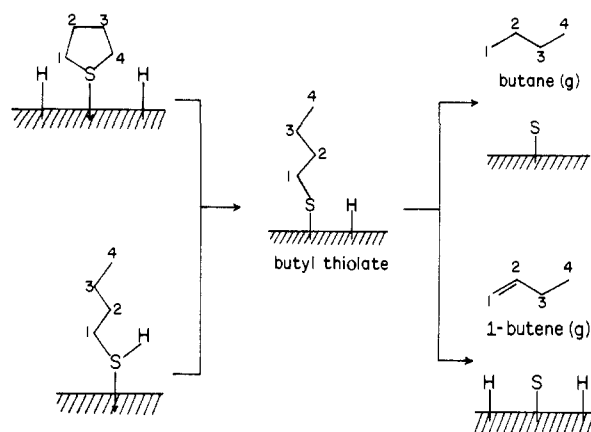


Figure 6. Proposed mechanism for the reaction of tetrahydrothiophene and 1-butanethiol on Mo(110).

surface reaction as outlined in the mechanism depicted in Figure 6. Tetrahydrothiophene is proposed to bond to the surface as a Lewis base through one of the two lone pairs on the sulfur, analogous to that proposed on the basis of ultraviolet photoemission studies of tetrahydrothiophene on Cu(100).⁵ Tetrahydrothiophene has also been proposed to bond to W(211) in a similar fashion.⁶ Hydrogenation of molecularly bound tetrahydrothiophene below 300 K occurs at one of the carbons located α to the sulfur to produce adsorbed butyl thiolate, as has been suggested on W(211).⁶ 1-Butanethiol is also proposed to bond to the Mo(110) surface as a Lewis base. Sulfur-hydrogen bond scission occurs first, at a temperature below 300 K, to give surface hydrogen and the adsorbed butyl thiolate. This assertion is substantiated by previous investigations of methanethiol on Pt(111),⁸ W(211),⁹ and Cu(100).¹⁰ It is also supported by the known low-temperature (below 300 K) O-H bond-breaking reactions of alkyl alcohols on Mo(100).^{20,21} The S-H bond energy (approximately 88 kcal/mol)²² is smaller than the O-H bond energy (102 kcal/mol) in alkyl alcohols.²³ Thus, thermodynamic considerations and the documented formation of alkoxides on transition-metal surfaces support the proposal of S-H bond scission as the first step in the temperature-programmed reaction of 1-butanethiol on Mo(110).

The butyl thiolate may undergo hydrogenation or dehydrogenation. At low temperatures (below 360 K) the surface hydrogen concentration is relatively high. Hydrogenation of the butyl thiolate at the α position with accompanying C-S bond breaking results in the formation of butane, observed in the temperature range of 300–360 K, depending on the surface hydrogen atom coverage and the adsorbate. At the end of this temperature range, desorption-limited hydrogen evolution from the surface commences. The surface hydrogen concentration drops, and the hydrogenation reaction to form butane becomes statistically unlikely. Instead, selective dehydrogenation at the carbon β to the sulfur atom in the butyl thiolate produces 1-butene. β -Dehydrogenation is the only simple mechanism by which the adsorbed thiolate can react to yield butene.

This mechanism predicts the selective formation of 1-butene. Because a quadrupole mass spectrometer cannot reliably distinguish between butene isomers, this prediction cannot be tested. 1-Butene is thermodynamically the least stable of the three butene isomers, and transition metals are often good olefin isomerization catalysts.²⁴ Thus, the selective production of 1-butene may not occur if the time scale for isomerization is comparable to the time scale for desorption. Because the butene peak is reaction limited, this seems unlikely. We note that the selective formation of 1-butene from 1-butanethiol adsorbed on evaporated nickel films

(18) $R_{S/Mo}$ is defined as the ratio of the following Auger signals: [Mo(LMM, 148 eV) + S(KLL, 152 eV)]/[Mo(LMM, 186 eV) + Mo(LMM, 221 eV)]. The sulfur signal overlaps with the Mo signal at 148 eV, but at these high sulfur coverages, the contribution of the 148-eV peak is negligible.

(19) The packing efficiencies were estimated by constructing models of tetrahydrothiophene and 1-butanethiol. The following bond lengths were assumed: C-C, 1.54 Å; C-H, 1.07 Å; C-S, 1.81 Å; S-H, 1.34 Å. The following van der Waals radii were assumed: C, 1.60 Å; H, 1.20 Å; S, 1.85 Å. Tetrahedral bond angles were also assumed. Only the most efficient packing arrangement was considered. 1-Butanethiol has a greater packing efficiency because the straight carbon chain can be directed away from the surface.

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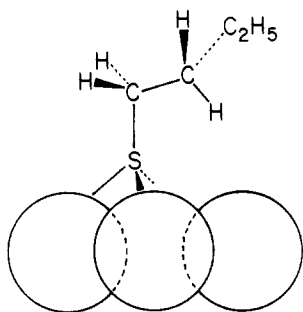


Figure 7. Proposed structure of the butyl thiolate intermediate.

at high pressure has been reported.⁷

The structures of discrete transition-metal complexes containing thiolate ligands provide information about the possible geometries of surface thiolates. In organometallic cluster compounds where there is bonding between the cluster metal atoms, the sulfur of a thiolate ligand usually bonds to achieve maximum metal coordination. For instance, in $\text{HFe}_3(\text{CO})_9(\text{S}-i\text{-C}_3\text{H}_7)$ the isopropyl thiolate group is located 1.50 Å above the plane of the three iron atoms, approximately equidistant from each.²⁵ The bonding around sulfur is nearly tetrahedral. Consequently, the S-C bond vector is perpendicular to the plane of the iron atoms. This compound is considered to be an appropriate organometallic analogue, and it is used to construct a plausible model for the Mo(110) butyl thiolate. In Figure 7 is shown a scale model of the proposed butyl thiolate intermediate. The carbon-sulfur, carbon-carbon, and carbon-hydrogen bond lengths are considered to be unperturbed from the gas-phase 1-butanethiol molecule, as was observed in $\text{HFe}_3(\text{CO})_9(\text{S}-i\text{-C}_3\text{H}_7)$. The bond angles of the thiolate group are assumed to be tetrahedral. By analogy to inorganic and organometallic compounds, a Mo-S distance of 2.44 Å is assumed.²⁶ The sulfur is placed in a pseudo-threefold position, on one side of one of the hourglass troughs present on a (110) bcc surface. The sulfur is equidistant from three Mo atoms, 1.79 Å above the surface plane. This geometry predicts a Mo-C_α distance of 3.97 Å, considerably greater than the van der Waals' sum of 2.96 Å. Hydrogen atoms have a van der Waals' diameter of 2.4 Å, so a surface hydrogen atom could access without difficulty C_α in the hydrogenation step that leads to butane. Therefore, a result of this geometry is that α-hydrogenation is an entirely reasonable process. Another direct result of this geometry is that the hydrogen atoms bonded to C_α are directed away from the surface. The shortest Mo-H_α distance is 3.98 Å. These are the only thiolate hydrogens sterically unlikely to interact with the surface. The hydrogen atoms located β to sulfur, by contrast, are directed toward the surface. The shortest Mo-H_β internuclear distance is 3.33 Å, fully 0.65 Å closer than the α hydrogens. A modest 20° tilt of the C-S bond vector brings one of the β-hydrogens within 2.35 Å of a Mo atom. This is less than 2.56 Å, the sum of the van der Waals' radii of bulk molybdenum and hydrogen. Such a tilt may be the step that leads to C-H_β dehydrogenation and 1-butene formation. While the microscopic details of the geometry of the intermediate of the mechanism are undetermined, we do suggest that this is a reasonable structure for the thiolate intermediate and that the steric requirements for α-hydrogenation and β-dehydrogenation are not demanding.

The high-temperature hydrogen peak appears just at the tetrahydrothiophene or 1-butanethiol exposure at which hydrocarbon production is first detected. This fact suggests that the intermediate which decomposes to butane and butene also reacts to form the fragment which eventually decomposes to give β₂-hydrogen. We therefore propose that a fraction of the butyl thiolate intermediate does not decompose to butane or butene. It instead decomposes to give the reaction-limited hydrogen detected at the far edge of the β₁-hydrogen peaks and an irreversibly bound hydrocarbon fragment. The irreversibly bound fragment then

decomposes at 565 K (tetrahydrothiophene) or 585 K (1-butanethiol) to β₂-hydrogen and surface carbon and sulfur. The nature of the irreversibly bound fragment is unknown. The β₂-H₂ formation peak is similar to that observed from thiophene on both Mo(100)²⁷ and Mo(110),² suggesting that the hydrogen-bearing fragment is similar in the three cases. Near edge X-ray absorption fine structure and electron energy loss spectra of thiophene on Pt(111)²⁸ and electron energy loss spectra of thiophene on Mo(100)²⁹ have been interpreted in terms of an unsaturated C₄-metallacyclic structure. The formation of a metallacycle from 1-butanethiol would be unusual and surprising, however. Spectroscopic studies, namely X-ray photoemission and high resolution electron energy loss spectroscopies, are planned to characterize the nature of the irreversibly bound fragment on the Mo(110) surface.

The deuterium preadsorption experiments support the proposed reaction mechanism. The first step in the temperature-programmed reaction of tetrahydrothiophene is hydrogenation of the heterocyclic ring. Both hydrocarbons are formed by way of a mechanism which involves hydrogenation. Therefore, both butane and butene must incorporate surface deuterium, as is observed. The first hydrogenation step is not required in the temperature-programmed reaction of 1-butanethiol, so butene is formed without any hydrogenation steps. No deuterium incorporation is expected in the butene formed from 1-butanethiol, and none is detected. Butane formation from 1-butanethiol by this mechanism requires only one hydrogenation step. At most one deuterium atom should be incorporated into the butane. This too is observed.

The selectivity for hydrogenation vs. dehydrogenation is expected to depend upon the coverage of atomic hydrogen, as is observed. If hydrogen is preadsorbed on Mo(110) to saturation, the butane/butene ratio from tetrahydrothiophene increases by a factor of 6, from 0.7 to 4.3. The butane/butene yield from 1-butanethiol is higher still, since the coverage of atomic hydrogen must necessarily be at least equal to the coverage of butyl thiolate. Thus, relatively more of the butyl thiolate is hydrogenated to butane if 1-butanethiol is the adsorbate and the butane/butene ratio is 4.6:1.0.

The greater hydrocarbon yield for reaction of 1-butanethiol compared to tetrahydrothiophene on the Mo(110) surface is attributed to three differences: (1) the thiol hydrogen on 1-butanethiol which results in a higher surface hydrogen concentration, (2) the larger saturation coverage of 1-butanethiol due to packing considerations, and (3) the fact that the first hydrogenation step is unnecessary for 1-butanethiol to form hydrocarbons.

Conclusions

Tetrahydrothiophene and 1-butanethiol react to form dihydrogen, butane, and 1-butene on Mo(110). Tetrahydrothiophene reversibly bonds to Mo(110) at high coverage, but 1-butanethiol does not. The similarity in the reaction energetics for hydrocarbon formation from the two molecules suggests that they decompose by way of the same intermediate. The intermediate is proposed to be a surface butyl thiolate. α-Hydrogenation of tetrahydrothiophene and simple S-H bond scission in 1-butanethiol yield the surface thiolate. The butyl thiolate undergoes hydrogenation to butane or dehydrogenation to 1-butene, depending on the concentration of surface hydrogen. This mechanism is proposed as a possible hydrodesulfurization pathway, at least for hydrogen-rich organic molecules.

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Registry No. Mo, 7439-98-7; H₂, 1333-74-0; 1-butanethiol, 109-79-5; tetrahydrothiophene, 110-01-0; thiophene, 110-02-1.

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