

Desulfurization of Saturated C₃S Molecules on Mo(110): The Effect of Ring Strain

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Abstract: The reactions of trimethylene sulfide (c-C₃H₆S) and 1-propanethiol (C₃H₇SH) have been investigated on Mo(110) under ultrahigh vacuum using temperature-programmed reaction spectroscopy and Auger electron spectroscopy. Deuterium preadsorption experiments were conducted in conjunction with temperature-programmed reaction spectroscopy to deduce some mechanistic details of the reactions. Desulfurization reactions of both molecules to produce propane and propene were observed in the temperature range of 300–350 K, with propane production preceding propene production. In addition, trimethylene sulfide decomposed to form cyclopropane at 190 K. Both trimethylene sulfide and 1-propanethiol reacted on Mo(110) to produce gaseous dihydrogen in two peaks at approximately 350 and 540 K, as well as surface carbon and sulfur. Small amounts of reversibly adsorbed 1-propanethiol desorbed from Mo(110) between 175 and 200 K. Auger electron spectroscopy measurements suggest that approximately 50% of chemisorbed trimethylene sulfide decomposed to form hydrocarbons, while 70% of irreversibly chemisorbed 1-propanethiol decomposed to form hydrocarbons. The decomposition of trimethylene sulfide to cyclopropane is postulated to occur by one of three pathways. One of these pathways is entirely intramolecular, and the other two involve metallacycle transition states or intermediates. Trimethylene sulfide and 1-propanethiol are proposed to form propane and propene by way of a surface propyl thiolate intermediate, in a fashion similar to the reactions of tetrahydrothiophene and 1-butanethiol on Mo(110). The possible contributions of ring strain to the energetics and selectivity of the desulfurization reactions are discussed.

Covalently bound sulfur is a major contaminant of nearly all crude fossil fuels.¹ The presence of sulfur is undesirable for two reasons. First, sulfur poisons the catalysts that accomplish many useful reactions, such as naphtha re-formation.² Also, the sulfur oxides produced during combustion of petroleum products are thought to contribute to acid rain.³ The catalytic removal of sulfur from petroleum feedstocks is therefore a process of considerable industrial importance. These catalytic reactions are collectively referred to as hydrodesulfurization.

Hydrodesulfurization reactions are generally carried out over sulfided, molybdenum-based catalysts. There is some agreement about the nature of these catalysts. For instance, the active sites of molybdenum-catalyzed hydrodesulfurization reactions are almost certainly edge or defect sites on a MoS₂-like phase.⁴ Considerably less is understood about the molecular level reaction mechanism(s) by which hydrodesulfurization occurs. In particular, there is controversy over the relative order and energetics of the C–S bond scission and C–H bond-formation processes.⁵

The reactions of sulfur-containing hydrocarbons on single-crystal transition metal surfaces are potentially useful models for hydrodesulfurization. We have recently reported the desulfurization under ultrahigh vacuum of the saturated C₄S molecules tetrahydrothiophene and 1-butanethiol on Mo(110).⁶ We proposed a mechanism to account for the formation of butane and butene from both tetrahydrothiophene and 1-butanethiol. The present work is concerned with the reactions of trimethylene sulfide and 1-propanethiol on Mo(110). Trimethylene sulfide and 1-propanethiol are the C₃ analogues of tetrahydrothiophene and 1-butanethiol. The investigation of these C₃ molecules was motivated by a desire to understand how properties of the sulfur-containing molecule, such as ring strain, affect reactivity.

The transition metal catalyzed reactions of trimethylene sulfide and trimethylene sulfide derivatives have been studied before. For instance, Raney nickel is known to catalyze the desulfurization of trimethylene sulfide derivatives to olefins and cyclopropanes.⁷

We are unaware, however, of any mechanistic studies of these reactions. Molybdenum atoms react with trimethylene sulfide to give two products: propene and cyclopropane.⁸ The nickel-catalyzed desulfurization of 1-propanethiol to propene and propane has also been reported.⁹ There have been to our knowledge no reports of the reactions of trimethylene sulfide with single-crystal transition metal surfaces. A study of the low-energy electron diffraction patterns formed on adsorption of 1-propanethiol on Ni(111) has been published.¹⁰ However, 1-propanethiol reactivity was not investigated in these studies.

Experimental Section

All experiments were performed in one of two virtually identical ultrahigh-vacuum systems which were described in detail previously.^{6,11} The working base pressure was always less than or equal to 3×10^{-10} torr. The methods of crystal preparation and cleaning in vacuo were identical with those described previously. As before, crystal cleanliness and order were monitored with retarding field Auger electron spectroscopy and low-energy electron diffraction, respectively.

Temperature-programmed reaction experiments were performed using radiative heating as described before.⁶ The chamber described in ref 6 was used to record the temperature-programmed reaction data which were integrated and are summarized in Figures 2 and 5 (vide infra). The heating rates were approximately constant, with $dT/dt = 16 \pm 1$ K/s between 120 and 750 K. This chamber was also used to record the Auger electron spectroscopy data presented in Figure 3. The chamber described in ref 10 was used to record the temperature-programmed reaction data reproduced in Figures 1 and 4, and to record the deuterium preadsorption experiments (vide infra). The heating rates in this chamber were not constant. There was a sharp, nonlinear decrease in rate as the crystal heated. At 120 K $dT/dt = 15$ K/s, and at 750 K $dT/dt = 5$ K/s. In general, approximately six masses were monitored during a temperature-programmed reaction experiment. However, in several experiments, all masses between 12 and 90 were monitored in a single temperature-programmed reaction experiment to check for unanticipated products, using a computer program described before.¹² Temperature-programmed reaction data were obtained with a shielded mass spectrometer

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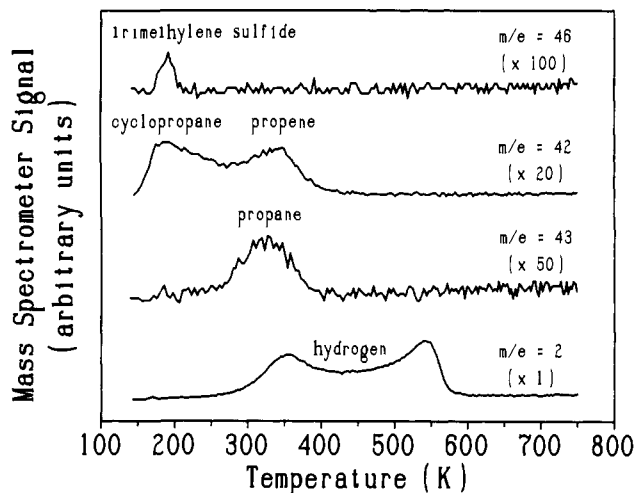


Figure 1. Temperature-programmed reaction spectra of trimethylene sulfide on Mo(110). The multiplication factors are referenced to hydrogen and are uncorrected for degree of fragmentation and ionization efficiency in the mass spectrometer. This spectrum corresponds to an exposure just to the onset of multilayer formation, as seen by the weak but sharp peak in the m/e 46 spectrum at 170 K.

designed to optimize detection of molecules desorbing normal to and from the center of the crystal surface, and to minimize the contribution of background reaction and/or desorption to the spectra.

Trimethylene sulfide (97%) and 1-propanethiol (99%) were obtained from Aldrich Chemicals. They were dried over sodium sulfate and distilled under an atmosphere of dry nitrogen. Their purity was verified by 1H NMR and mass spectrometry. The trimethylene sulfide and 1-propanethiol were degassed before use each day by several freeze/pump/thaw cycles. All gases (O_2 , H_2 , D_2 , propane, cyclopropane, and propene) were obtained from Matheson and used without further purification.

Gases were admitted to the chamber using directed dosers described previously,⁶ with the crystal maintained at 130 K unless otherwise specified. Exposures are given in units torr·s. A torr·s is defined as the product of the dosing time and the pressure maintained 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.

Results

Trimethylene Sulfide. Temperature-programmed reaction data obtained after trimethylene sulfide adsorption are presented in Figure 1. The trimethylene sulfide exposure resulting in the temperature-programmed reaction spectrum reproduced in Figure 1 corresponds to the onset of trimethylene sulfide multilayer growth. The five volatile products detected were dihydrogen (m/e 2) in two peaks labeled β_1 and β_2 at 350 and 540 K, respectively, propane (m/e 43) at 320 K, cyclopropane (m/e 42) at 190 K, propene (m/e 42) at 345 K, and trimethylene sulfide (m/e 46) at 180 K. Trimethylene sulfide desorption appeared only for exposures large enough to saturate all other product peaks. The sharp, low-temperature trimethylene sulfide peak never saturated. It is attributed to desorption of trimethylene sulfide multilayers and will not be discussed further. The temperature of the cyclopropane peak (190 K) is quite close to the adsorption temperature (130 K), suggesting that some cyclopropane production may have occurred upon trimethylene sulfide adsorption. However, we were unable to detect any cyclopropane production during trimethylene sulfide adsorption.

The masses presented in Figure 1 are generally the most intense observed for which only one peak contributed to the signal. Propane has a molecular ion (m/e 44) and a cracking fraction (m/e 29) that are more intense than the $M - 1$ ion (m/e 43). However, the background m/e 44 signal due to CO_2 and the spillover m/e 28 signal made the signal-to-noise ratio smaller if m/e 44 or 29 was detected. Cyclopropane and propene have very similar cracking patterns in our mass spectrometer, so they were necessarily detected together. The relative yields in our mass spectrometer of the six most intense ions of authentic samples of

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

molecule	mass/charge (% yield)					
	46	28	27	26	39	41
trimethylene sulfide	46	28	27	26	39	41
	(100)	(50)	(45)	(32)	(29)	(24)
1-propanethiol	27	41	42	43	47	39
	(100)	(90)	(76)	(64)	(57)	(49)
propane	29	28	27	44 ^c	39	43
	(100)	(74)	(49)	(21)	(20)	(18)
cyclopropane	41	42 ^c	39	40	27	38
	(100)	(95)	(79)	(34)	(22)	(18)
propene	41	39	42 ^c	27	40	38
	(100)	(81)	(63)	(54)	(31)	(24)

^a Measured using the experimental configuration described in this work. ^b The molecular ions of trimethylene sulfide (m/e 74) and 1-propanethiol (m/e 76) are less than 10% as intense as the most intense ion in their respective mass spectra. ^c The molecular ion.

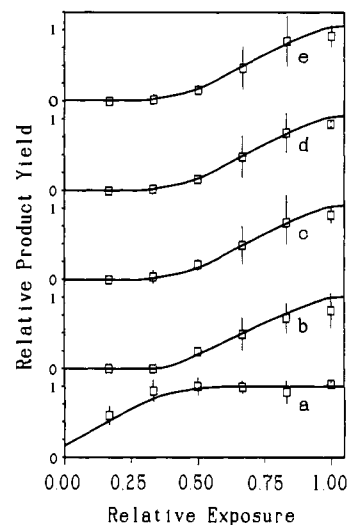


Figure 2. Fractional temperature-programmed reaction yield of (a) β_1 -dihydrogen, (b) β_2 -dihydrogen, (c) propane, (d) cyclopropane, and (e) propene vs. trimethylene sulfide exposure. The product yields are referenced to their saturation values. An exposure of 1.00 corresponds to reaction saturation and the onset of multilayer desorption. The error bars are statistically derived and are the average of five experiments.

propane, cyclopropane, propene, and trimethylene sulfide are shown 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 propane, cyclopropane, propene, and trimethylene sulfide agreed with the ion yields shown in Table I. In particular, the m/e 41:42 ratio of the peak we assign as cyclopropane was 1.2, while the experimentally determined m/e 41:42 ratio of cyclopropane in our mass spectrometer was 1.1. The 41:42 ratio of the peak we assign as propene was 1.8, while the experimentally determined propene 41:42 ratio was 1.6.

Figure 2 depicts the integrated peak intensities of the five observed products as a function of trimethylene sulfide exposure. The integrated intensities were measured with respect to time. The exposures and yields have been normalized to their reaction saturation values. The $(\beta_1 + \beta_2)\text{-}H_2$ /propane/cyclopropane/propene ratio at saturation was approximately 100:5:10:12. This ratio is calculated from the integrated temperature-programmed reaction peaks, corrected for ionization efficiency and transmission probabilities in the mass spectrometer.¹³ The large number of assumptions used in calculating the ratio makes it a crude estimate. Still, the ratio does demonstrate that approximately half of the trimethylene sulfide decomposed to yield hydrocarbon products.

Temperature-programmed reaction of low exposures of trimethylene sulfide (less than 5.0 torr·s = 0.33 saturation) resulted

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exclusively in irreversible decomposition. All carbon and sulfur remained on the surface. Dihydrogen evolution proceeded solely from the β_1 state(s). At exposures of 2.5 torr-s (0.17 saturation) molecular hydrogen evolved from the surface at 500 K. As the exposure increased the H_2 peak shifted down in temperature until at exposures of 5 torr-s (0.33 saturation), β_1 -hydrogen evolved at 440 K. At exposures of 7.5 torr-s (0.50 reaction saturation) a small new peak appeared in the β_1 temperature regime, at 330 K. The 330-K peak increased further in intensity with increasing trimethylene sulfide exposure, while the 400-K peak decreased in intensity. At reaction saturation the two peaks coalesced into one at 350 K. Because dihydrogen was found to desorb from clean Mo(110) between 400 and 500 K,¹⁴ the β_1 -hydrogen peak may arise from either a reaction-limited or desorption-limited process. That is, the rate-limiting step leading to β_1 -hydrogen may be identical with the step leading to hydrogen desorption from clean Mo(110) (desorption limited), or the rate-limiting step may be the decomposition of a separate surface intermediate or transition state (reaction limited). The nature of the β_1 - H_2 peak will be further discussed below.

For exposures greater than 5 torr-s, β_2 - H_2 was evident in the trimethylene sulfide temperature-programmed reaction spectra. At exposures corresponding to 0.50 saturation β_2 -dihydrogen appeared as a shoulder on the β_1 peak at 525 K. The β_2 peak increased in intensity and temperature with increasing trimethylene sulfide exposure. At reaction saturation the well-resolved β_2 - H_2 peak reached its maximum at 540 K. If the Mo(110) surface was saturated with trimethylene sulfide, heated to 475 K (the minimum between the β_1 and β_2 peaks), and cooled to 135 K, then only β_2 -hydrogen was detected in a subsequent temperature-programmed reaction experiment. Therefore, there can be no exchange between the β_1 and β_2 sites after all β_1 - H_2 has left the surface.

All three hydrocarbons (propane, cyclopropane, and propene) first appeared at trimethylene sulfide exposures greater than 5 torr-s (0.33 reaction saturation), the exposure at which β_2 - H_2 was also first detected. At trimethylene sulfide exposures of 7.5 torr-s (0.50 reaction saturation), propane evolved from the Mo(110) surface at 330 K. As the trimethylene sulfide exposure increased more propane was produced. The propane production temperature decreased with increasing trimethylene sulfide exposure up to reaction saturation (15 torr-s). At reaction saturation, the propane feature peaked at 320 K. The fact that the peak temperature decreased with increasing coverage is consistent with a second-order rate-limiting step in the pathway leading to propane production, although the temperature shift does not prove a second-order process. In contrast to the propane peak, the cyclopropane and propene peaks did not shift in temperature with increasing trimethylene sulfide exposure, consistent with a first-order rate-limiting step in the pathways that lead to cyclopropane and propene. At all exposures, cyclopropane and propene evolved from the surface at 190 and 345 K, respectively. They increased in intensity with increasing trimethylene sulfide exposure in a fashion identical with propane (see Figure 2). All hydrocarbon peaks are reaction limited. Temperature-programmed reaction of propane, cyclopropane, and propene adsorbed on Mo(110) result in molecular desorption at 155, 150, and 200 K, respectively.¹⁵

Auger electron spectroscopy was used to determine the C:S surface stoichiometry after temperature-programmed reaction of trimethylene sulfide to 750 K. There was no evidence for electron-stimulated desorption of carbon or sulfur during Auger measurements, or for diffusion of carbon or sulfur into the bulk crystal on heating the crystal during a temperature-programmed reaction experiment.¹⁶ The carbon/sulfur Auger ratio, $R_{C/S}$, is shown as a function of adsorbate exposure in Figure 3.¹⁷ For

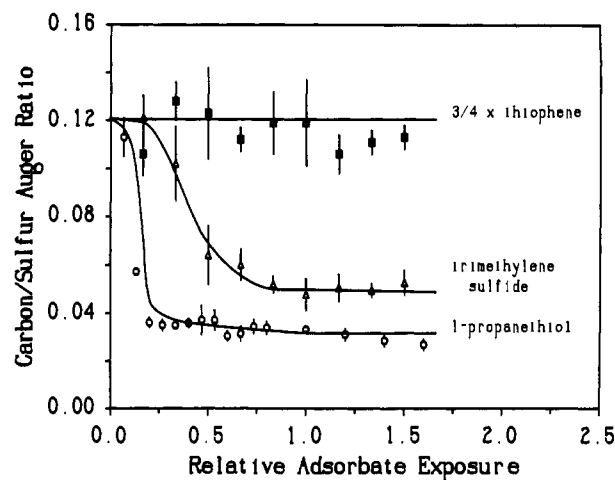


Figure 3. $R_{C/S}$, the C/S Auger ratio, after temperature-programmed reaction to a maximum temperature of 750 K vs. adsorbate dose. The ratios for the adsorbates thiophene (with $R_{C/S}$ multiplied by $3/4$), trimethylene sulfide, and l-propanethiol are represented by filled squares, triangles, and 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.

trimethylene sulfide exposures up to 5 torr-s (=0.33 reaction saturation), $R_{C/S} = 0.11 \pm 0.01$. In this coverage regime no hydrocarbons were produced during reaction. All of the carbon and sulfur remained on the surface after temperature-programmed reaction. Therefore, a value of $R_{C/S} = 0.11$ corresponds to a C_3S surface stoichiometry. This ratio is in excellent agreement with the anticipated C/S Auger ratio based on C/S calibrations derived from thiophene decomposition on Mo(110).¹⁸ Thiophene decomposed on Mo(110) to yield gaseous dihydrogen, surface carbon, and surface sulfur with no hydrocarbon product formation. For all thiophene exposures, $R_{C/S}$ measured after temperature-programmed reaction was 0.15 ± 0.1 . This value references a C_4S surface stoichiometry, so ($3/4 R_{C/S}$) after thiophene reaction should reference a C_3S surface stoichiometry. The value ($3/4 R_{C/S}$) after thiophene reaction is 0.11 ± 0.1 (Figure 3). The equivalence of $R_{C/S}$ after trimethylene sulfide reaction and ($3/4 R_{C/S}$) after thiophene reaction confirms that no hydrocarbon formation occurred for trimethylene sulfide exposures less than 5 torr-s (0.33 reaction saturation). Increasing trimethylene sulfide exposures resulted 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 was 0.05 ± 0.01 . Comparison of this value with the low exposure limit of 0.11 ± 0.01 allows a rough estimate of the fractional hydrocarbon yield. Approximately 45% of the trimethylene sulfide chemisorbed on Mo(110) decomposed to 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 propane, cyclopropane, and propene (see above). The Auger electron spectroscopy derived yield is considered to be a more reliable value owing to the large number of assumptions made in calculating the hydrocarbon yield from mass spectral data.

Hydrogen preadsorption experiments were performed to check for the sensitivity of the hydrogen and hydrocarbon peaks to surface hydrogen concentration. In these experiments, a saturation dose of hydrogen (120 torr-s) was preadsorbed as the Mo(110) crystal cooled from room temperature. After cooling to 135 K, trimethylene sulfide was adsorbed at an exposure greater than that required for reaction saturation. The crystal was then warmed

(14) Roberts, J. T.; Friend, C. M., unpublished results.

(15) Roberts, J. T.; Liu, A. C.; Friend, C. M., to be published.

(16) The Auger spectra did not significantly change on exposure to the electron beam for 15 min, while only 5 min was required to record an Auger spectrum. In addition, no differences in the Auger peaks were evident when the crystal was heated to 1200 K instead of 750 K, suggesting that diffusion into the crystal bulk does not occur.

(17) $R_{C/S}$ is defined as the ratio of the peak-to-peak height 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. The Mo(MNN) and S(LMM) derivative intensities were added because they overlap in energy and are impossible to deconvolute.

(18) Roberts, J. T.; Friend, C. M., submitted for publication in *Surf. Sci.*

Table II. Relative Intensities^a of Deuterated Hydrocarbon Products Produced from Reaction of Trimethylene Sulfide or 1-Propanethiol and Preadsorbed Deuterium

hydrocarbon product	adsorbate	
	trimethylene sulfide	1-propanethiol
cyclopropane- <i>d</i> ₀	1.0	
cyclopropane- <i>d</i> ₁	0.0	
propene- <i>d</i> ₀	1.0	1.0
propene- <i>d</i> ₁	0.7	0.0
propene- <i>d</i> ₂	0.0	0.0
propane- <i>d</i> ₀	1.0	1.0
propane- <i>d</i> ₁	1.3	0.6
propane- <i>d</i> ₂	0.7	0.0
propane- <i>d</i> ₃	0.0	0.0

^aThe intensities were measured as the peak heights of the molecular ion and are uncorrected for fragmentation in the mass spectrometer. The relative intensities are normalized to the hydrocarbon-*d*₀ peak.

to 180 K, so that the multilayers of trimethylene sulfide had desorbed. Subsequent to cooling to 135 K, a temperature-programmed reaction spectrum was recorded. The sulfur/molybdenum Auger ratios, $R_{S/Mo}$, measured after these experiments were identical within experimental error with those measured after temperature-programmed reaction without preadsorbed hydrogen. Thus, the amount of trimethylene sulfide chemisorbed on Mo(110) is unaffected by the presence of surface hydrogen. As expected, the β_1 -H₂ increased in intensity by a factor of 4, but the β_2 -hydrogen peak decreased in intensity by about one-third. The leading edge of the β_1 -H₂ peak increased much more than the far edge of the β_1 -H₂ peak. This is interpreted as evidence that the β_1 peak results from a superposition of reaction and desorption limited states, with the leading edge of the peak due mostly to desorption limited hydrogen. This conclusion will be further supported below. The temperature of the β_2 -H₂ peak decreased from 540 to 500 K.

If hydrogen was preadsorbed, the integrated intensity of the propane peak increased by a factor of 2, and the temperature maximum of the propane peak dropped from 220 to 200 K. By contrast, the cyclopropane peak did not change in yield or temperature maximum if hydrogen was preadsorbed. The propene peak, too, was unaffected by the presence of preadsorbed hydrogen. These results are consistent with a mechanism involving hydrogenation as the rate-limiting step leading to propane production. Furthermore, cyclopropane and propene production appear to be first-order processes, suggesting a mechanism whereby unimolecular decomposition of a surface bound fragment is rate limiting.

Deuterium preadsorption experiments were performed to probe for H-D exchange processes in the surface intermediates that yield dihydrogen, propane, cyclopropane, and propene. These experiments were conducted just as the hydrogen preadsorption experiments except that the trimethylene sulfide multilayers were not desorbed before temperature-programmed reaction.

The extent of deuterium production into the hydrocarbons produced during temperature-programmed reaction of deuterium and trimethylene sulfide on Mo(110) is summarized in Table II. Ions corresponding to propane-*d*₀, -*d*₁, and -*d*₂ were detected in the propane temperature formation regime. No propane-*d*₃ was detected. The reaction pathway leading to propane formation is therefore proposed to involve two hydrogenation steps by surface hydrogen. Only cyclopropane-*d*₀ was detected, suggesting that cyclopropane is formed by an intramolecular process. Ions corresponding only to propene-*d*₀ and -*d*₁ were detected in the propene temperature formation regime. Thus, propene formation requires one hydrogenation step by surface hydrogen.

All three possible hydrogen deuterium isotopic combinations were observed in the β_1 - and β_2 -dihydrogen 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 III. The β_1 -H₂, -HD, and -D₂ peak temperatures were approximately 350, 340, and 330 K, respectively. The β_1 -H₂ and -D₂ peaks were narrower when deuterium was preadsorbed than was the β_1 -H₂ peak when

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

isotopic combination	β_1	β_2
	H ₂	1.00
HD	0.87	0.24
D ₂	0.44	0.08

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

just trimethylene sulfide was adsorbed, but the β_1 -HD peak was nearly as wide as the β_1 -H₂ peak when just trimethylene sulfide was adsorbed. The β_1 -H₂ full width at half-maximum (fwhm) was 80 K when deuterium was not preadsorbed. If deuterium was preadsorbed, the β_1 -H₂ and -D₂ fwhm values were 50 K, while the β_1 -HD fwhm was 70 K. The leading edges of the β_1 -HD and -D₂ matched and were 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 240 K and of β_1 -H₂ at 260 K. By contrast, the far edges of the β_1 -H₂ and HD peaks matched and were higher in temperature than the far edge of the β_1 -D₂ peak. Our interpretation of the β_1 -hydrogen peak is identical with our interpretation of the β_1 -hydrogen peak from tetrahydrothiophene and 1-butanethiol on Mo(110).⁶ The β_1 -hydrogen peak 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 of β_1 -H₂, HD, and D₂ in deuterium preadsorption experiments. Also, there is no pronounced isotope effect for hydrogen desorbing from clean Mo(110).¹⁵

Preadsorbed deuterium, like preadsorbed hydrogen, suppressed the formation of the β_2 peak. The β_2 -dihydrogen peak exhibited 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.¹⁹ The peak temperatures for β_2 -H₂, -HD, and -D₂ were 500, 515, and 525 K, respectively. The β_2 H/D ratio was 1.4, while the β_1 H/D ratio was 2.1. Hence, proportionally less deuterium was incorporated into the β_2 peak. If the surface was saturated with trimethylene sulfide, heated to 475 K (the minimum between the β_1 and β_2 peaks), dosed to saturation with deuterium, and cooled to 135 K, then no HD or D₂ appeared in the β_2 peak. HD and D₂ appeared solely as β_1 -hydrogen. Therefore, deuterium incorporation occurs someplace along the decomposition pathway, but before formation of the intermediate which yields β_2 -hydrogen.

1-Propanethiol. Five gas-phase products were detected during the temperature-programmed reaction of 1-propanethiol on Mo(110): dihydrogen, propene, propane, 1-propanethiol, and di-1-propyl disulfide. No cyclopropane formation was detected from reaction of 1-propanethiol. Data from a typical temperature-programmed reaction experiment after adsorption of 1-propanethiol multilayers are reproduced in Figure 4. Dihydrogen (detected as m/e 2) evolved from the surface in a β_1 peak at 360 K and in a β_2 peak at 545 K. Propane (m/e 43) production reached a maximum at 280 K, and propene (m/e 42) was detected in a very broad peak centered at 320 K. Chemisorbed 1-propanethiol desorbed from the surface in small quantities at 200 K. Multilayers of 1-propanethiol desorbed at 155 K. In Figure 4 the large 1-propanethiol multilayer peak obscures the chemisorbed 1-propanethiol peak. The product identified as di-1-propyl disulfide appeared only at extremely large 1-propanethiol exposures (>10 reaction saturation), so it was not detected in the experiment recorded in Figure 4. It is attributed to a reaction in the multilayer

(19) The crystal temperature was measured with a W-5% Re/W-26% Re thermocouple, which is known to have a poor absolute calibration. However, the temperatures of H₂, HD, and D₂ production were measured during a single experiment. Thus, the isotope effect is genuine and not an experimental artifact.

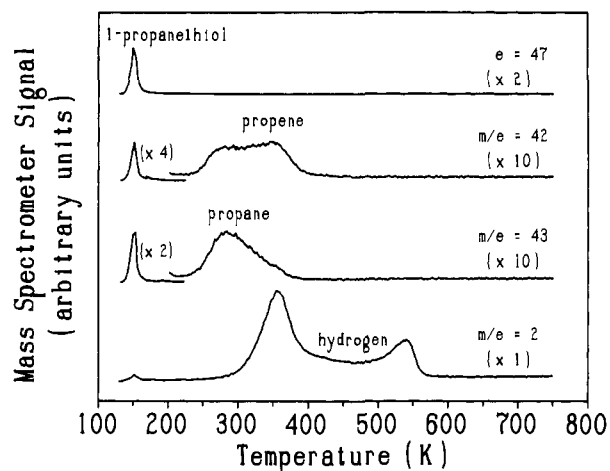


Figure 4. Temperature-programmed reaction spectra of 1-propanethiol on Mo(110). The multiplication factors are referenced to hydrogen and are uncorrected for degree of fragmentation and ionization efficiency in the mass spectrometer. This spectrum corresponds to an exposure of 1-propanethiol multilayers as is evident from the sharp peaks in the $m/e = 42, 43,$ and 47 spectra at 155 K. The multilayer peak obscures a small chemisorbed 1-propanethiol peak at 200 K.

and will not be discussed further.²⁰

As was the case with trimethylene sulfide, the masses presented in Figure 4 are generally the most intense observed for which only one peak contributed to the signal. Again, the relative ion yields of the peaks assigned as propane, propene, and 1-propanethiol agree within experimental error with the ion yields shown in Table I.

The dependences of the fractions β_1 -hydrogen, β_2 -hydrogen, propene, propane, and chemisorbed 1-propanethiol production on the relative 1-propanethiol dose are shown in Figure 5. At saturation exposures, the $(\beta_1 + \beta_2)$ -dihydrogen/propane/propene/1-propanethiol ratio, calculated from the integrated peaks and corrected for fragmentation in the mass spectrometer, was approximately 100:60:20:2.¹³ Hence, approximately 75% of irreversibly adsorbed 1-propanethiol decomposed to form gaseous hydrocarbons. The total hydrocarbon yield from 1-propanethiol was about 1.75 times the yield from trimethylene sulfide. The $(\beta_1 + \beta_2)$ -dihydrogen yield from reaction of 1-propanethiol was not significantly different from the total dihydrogen yield from reaction of trimethylene sulfide. However, the β_1 -H₂/ β_2 -H₂ ratio measured for trimethylene sulfide was 1.25, but the β_1 -H₂/ β_2 -H₂ ratio measured for 1-propanethiol was 0.75.

At low 1-propanethiol exposures (<5 torr-s = 0.07 reaction saturation) total decomposition of the adsorbate was the only reaction pathway detected. Dihydrogen was produced in the β_1 region of the temperature-programmed reaction spectrum in two poorly resolved peaks at 325 and 425 K, and in a weak shoulder at 490 K. The dihydrogen peaks at 325 and 425 K increased rapidly in intensity with increasing 1-propanethiol exposure and coalesced into a single broad peak at 360 K at 1-propanethiol exposures of 10 torr-s (0.13 reaction saturation). The β_1 -H₂ peak was virtually saturated at exposures of 15 torr-s (0.20 reaction saturation). The β_2 -H₂ feature first appeared at exposures of 0.13 reaction saturation as a very weak shoulder on the β_1 -H₂ peak, at 530 K. The β_2 feature became well resolved and increased in intensity with increasing 1-propanethiol exposure. At exposures of 40 torr-s (0.47 reaction saturation) the β_2 -H₂ peak was saturated. Its temperature at saturation was 545 K.

Coincident with the appearance of the β_2 -H₂ feature were the propane and propene peaks. The two hydrocarbon peaks first appeared at 1-propanethiol exposures of 0.13 reaction saturation. They increased in intensity with increasing adsorbate exposure

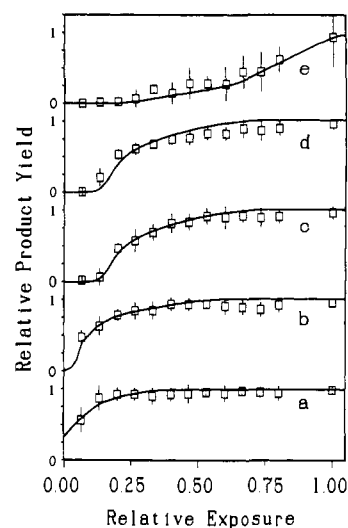


Figure 5. Fractional temperature-programmed reaction yield of (a) β_1 -dihydrogen, (b) β_2 -dihydrogen, (c) propane, (d) propene, and (e) 1-propanethiol vs. trimethylene sulfide exposure. The product yields are referenced to their saturation values. An exposure of 1.00 corresponds to reaction saturation and the onset of multilayer desorption. The error bars are statistically derived and are the average of five experiments.

in an identical fashion, as shown in Figure 5. At exposures of 55 torr-s (0.73 reaction saturation) the two hydrocarbon peaks were saturated. Propane first appeared as a symmetric peak centered at 310 K. The peak temperature shifted to lower temperature with increasing exposure until reaction saturation when the desorption maximum was located at 280 K. The propane peak also became asymmetric, as shown in Figure 4. Propene first evolved in a symmetric peak at 315 K. The peak broadened and flattened with increasing adsorbate exposure until at reaction saturation the propene peak was at its maximum intensity between 275 and 350 K. Approximately 50% of the low-temperature region of the propene temperature-programmed reaction spectrum is due to the superposition of the propane peak since propane cracks at m/e 42.

At exposures of 30 torr-s (0.40 reaction saturation) and greater, chemisorbed 1-propanethiol desorbed from Mo(110). The desorption temperature was 200 K at exposures of 0.40 reaction saturation, but it shifted down with increasing 1-propanethiol exposure. At reaction saturation 1-propanethiol desorbed from Mo(110) at 175 K.

Auger electron spectroscopy was used to determine the surface C:S stoichiometry after temperature-programmed reaction of 1-propanethiol as described for trimethylene sulfide. In Figure 3 $R_{C/S}$ is plotted vs. the relative 1-propanethiol dose. For low 1-propanethiol exposures (<0.10 reaction saturation), $R_{C/S} = 0.11 \pm 0.01$, indicating a C₃S surface stoichiometry consistent with the fact that no hydrocarbons are produced in this exposure regime. As the exposure increased, $R_{C/S}$ decreased as a result of hydrocarbon formation reaching a value of 0.03 ± 0.01 at reaction saturation. This ratio suggests that at reaction saturation approximately 70% of the irreversibly bound 1-propanethiol reacted to form hydrocarbons. This value agrees with that calculated above using the integrated mass spectral intensities.

The sulfur/molybdenum Auger ratio, $R_{S/Mo}$,²¹ measured after temperature-programmed reaction of 1-propanethiol was 1.4 ± 0.1 at saturation. The value of $R_{S/Mo}$ measured after trimethylene sulfide reaction was 1.2 ± 0.1 . Therefore, 1-propanethiol deposited about 1.2 times as much sulfur as trimethylene sulfide in the high-exposure limit. This difference suggests that, compared to trimethylene sulfide, a greater number of 1-propanethiol molecules are adsorbed on the Mo(110) surface at saturation. This is at-

(20) The amount of di-1-propyl disulfide did not increase as a function of residence time of the trimethylene sulfide in the dosing manifold, precluding reaction in the doser giving rise to the disulfide. In addition, no evidence for a disulfide impurity was obtained using ¹H NMR or mass spectrometry.

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

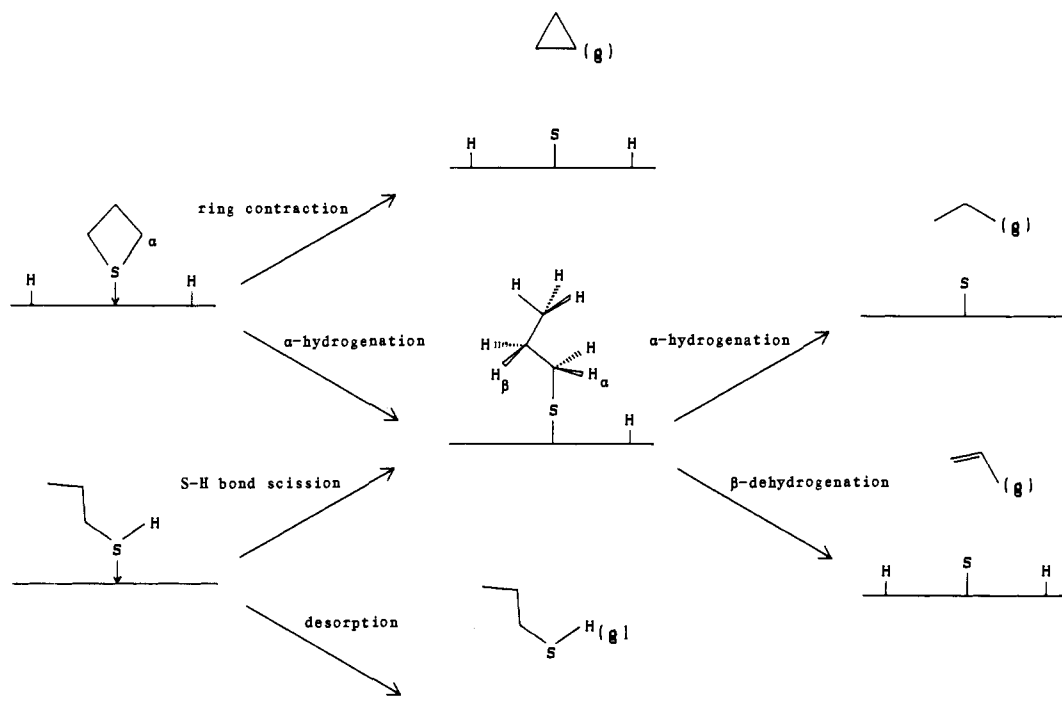


Figure 6. Proposed mechanism for the reactions of trimethylene sulfide and 1-propanethiol on Mo(110).

tributed to the relative packing efficiencies of trimethylene sulfide and 1-propanethiol. If 1-propanethiol and trimethylene sulfide are 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-propanethiol vs. trimethylene sulfide is approximately 1:1.2.²² The sulfur/molybdenum Auger ratio on Mo(110)-p(2×2)-S has been determined to be 1.2 ± 0.1 .¹⁸ The sulfur coverage on Mo(110)-p(2×2)-S was taken to be 0.25 monolayer.²³ Using the -p(2×2)-S as a reference state, trimethylene sulfide and 1-propanethiol were respectively estimated to deposit approximately 0.25 and 0.30 monolayer of sulfur on Mo(110) at reaction saturation.

Hydrogen preadsorption experiments were again performed to check for the sensitivity of the hydrogen and hydrocarbon peaks to surface hydrogen concentration. As was observed for trimethylene sulfide, hydrogen preadsorption did not change the total 1-propanethiol uptake, as measured by $R_{S/Mo}$. The β_1 -H₂ increased in intensity by a factor of 2, but the β_2 -dihydrogen peak decreased in intensity by about one-half. The leading edge of the β_1 -H₂ peak increased much more than the far edge of the β_1 -H₂ peak, just as it did when hydrogen was preadsorbed with trimethylene sulfide. The temperature of the β_2 -H₂ peak decreased from 545 to 505 K. Neither the temperatures nor the integrated intensities of the propane and propene peaks changed if hydrogen was preadsorbed.

The extent of deuterium incorporation into the hydrocarbons produced during temperature-programmed reaction of coadsorbed deuterium and trimethylene sulfide on Mo(110) is summarized in Table II. Ions corresponding to propane- d_0 and - d_1 were detected in the propane temperature formation regime. In contrast to the reaction of trimethylene sulfide, no propane- d_2 was detected, consistent with a reaction pathway leading to propane formation which involves a single hydrogenation step by surface hydrogen. Only propene- d_0 is detected; no deuterated propene products were

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

isotopic combination	β_1	β_2
H ₂	1.00	0.41
HD	0.51	0.08
D ₂	0.13	0.01

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

observed. Thus, propene formation does not involve hydrogenation by surface hydrogen atoms.

Surface deuterium was not incorporated into chemisorbed 1-propanethiol. Reversibly bound 1-propanethiol is therefore associatively chemisorbed.

Deuterium preadsorption and subsequent reaction of 1-propanethiol on Mo(110) results in deuterium incorporation into all areas of the dihydrogen temperature-programmed reaction spectrum. The β_1 and β_2 peaks from the reaction of 1-propanethiol with preadsorbed deuterium are similar to the β_1 and β_2 peaks from the reaction of trimethylene sulfide with preadsorbed deuterium. The β_1 -H₂, -HD, and -D₂ peaks are 350, 340, and 335 K. The β_2 -H₂, -HD, and -D₂ peak temperatures were 510, 520, and 530 K. The relative β_1 and β_2 product yields are shown in Table IV. The β_1 and β_2 H/D ratios are 2.4 and 5.4, respectively. Proportionally more deuterium was incorporated into the β_1 peak. The β_1 -H₂ peak is again interpreted to be a superposition of two peaks: desorption-limited dihydrogen accounts for the leading edge of the β_1 peak, and reaction-limited dihydrogen comprises the far edge of the β_1 peak.

Discussion

Except for the cyclopropane peak, the temperature-programmed reaction of trimethylene sulfide is very similar to that of 1-propanethiol. The dihydrogen traces are very similar, with two temperature regimes of formation: β_1 and β_2 . Furthermore, both molecules decompose to hydrocarbons in the same temperature regime, with propane preceding propene evolution. The correspondence in the trimethylene sulfide and 1-propanethiol reactions suggests a mechanism whereby they decompose to propane and propene by way of the same intermediate. We propose a general mechanism for the desulfurization of trimethylene sulfide and

(22) The packing efficiencies were estimated by constructing models of trimethylene sulfide and 1-propanethiol. The following bond lengths (Å) were assumed: C-C, 1.54; C-H, 1.07; C-S, 1.81; S-H, 1.34. The following van der Waals' radii (Å) were assumed: C, 1.60; H, 1.20; S, 1.85. Tetrahedral bond angles were also assumed. The relative surface areas were determined by projecting onto a plane an image of a model of the adsorbate molecule in its assumed bonding geometry. The projected image was integrated, and the integral was taken as the relative excluded surface area.

(23) Sanchez, A.; De Miguel, J. J.; Martinez, E.; Miranda, A. *Surf. Sci.* **1986**, *171*, 157-169.

1-propanethiol on Mo(110) which is outlined in Figure 6. The mechanism accounts for all details of the trimethylene sulfide and 1-propanethiol reactions, including the formation of cyclopropane. It is very similar to the reaction mechanism we previously postulated for tetrahydrothiophene and 1-butanethiol,⁶ suggesting that the proposed desulfurization mechanism is somewhat general.

At low exposures, irreversible and total decomposition is the only reaction pathway available to both trimethylene sulfide and 1-propanethiol. All carbon and sulfur remain on the surface after temperature-programmed reaction, as confirmed by Auger electron spectroscopy. Gas-phase dihydrogen, formed by recombination of surface hydrogen atoms, is the sole volatile product. Dehydrogenation of both molecules must be complete below 500 K, based on the molecular hydrogen formation peak.

At high exposures of either trimethylene sulfide or 1-propanethiol, not all of the adsorbate undergoes complete decomposition. Some trimethylene sulfide and 1-propanethiol bond to the surface as Lewis bases, through one of the two lone pairs of electrons on sulfur. This sort of bonding scheme has been suggested before for cyclic sulfides and thiols adsorbed on transition metal surfaces.^{6,24} Furthermore, innumerable discrete transition metal complexes are known in which sulfides and thiols bond to a metal as a Lewis base.²⁵

The first step in the temperature-programmed reaction of 1-propanethiol is dissociation of the S-H bond to the propyl thiolate intermediate and surface hydrogen, as shown in Figure 6. The temperature of this transformation is undefined, but it must be between 130 and 225 K. The lower bound of 130 K is the adsorption temperature, and the upper bound of 225 K corresponds to the temperature at which propane formation commences. Formation of surface thiolate complexes from methanethiol has been suggested on Pt(111),²⁶ W(211),²⁷ and Cu(100).²⁸ Also, formation of surface alkoxides from alcohols on Mo(100) has been shown to occur below 300 K.²⁹ The S-H bond energy of alkyl thiols is approximately 92 kcal/mol,³⁰ lower than the O-H bond energy of 102 kcal/mol in alkyl alcohols.³¹ Thus, thermodynamic considerations and the documented formation of surface alkoxides from alcohols further support the proposal of S-H bond scission as the first step in the temperature-programmed reaction of 1-propanethiol on Mo(110).

At temperatures between 130 and 190 K, at least three competing reaction channels are available to adsorbed trimethylene sulfide. Decomposition to surface hydrogen, surface carbon, and surface sulfur is the predominant initial pathway since for low trimethylene sulfide coverages only decomposition is observed. Hydrogenation of one of the carbon-sulfur bonds to produce a surface propyl thiolate (C_3H_7S) intermediate is a competing pathway. The propyl thiolate is schematically depicted in Figure 6. The surface hydrogen necessary for this hydrogenation step originates from the fraction of the trimethylene sulfide that has at least started to decompose to surface carbon, sulfur, and hydrogen by the first reaction channel. The third reaction channel available to trimethylene sulfide adsorbed on Mo(110) is intramolecular cyclopropane formation.

Our observation of cyclopropane evolution during temperature-programmed reaction of trimethylene sulfide on Mo(110) may seem surprising. Because of ring strain, cyclopropane has a high enthalpy of formation, 12.8 kcal/mol.³² Moreover, the temperature at which cyclopropane is produced is exceedingly low, 190 K. We are convinced that the product we detect at 190 K

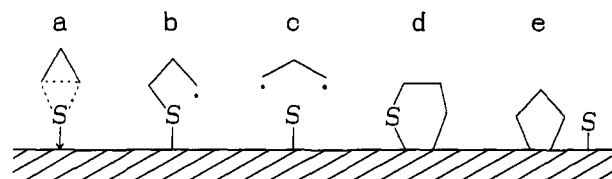


Figure 7. Structures of possible transition states and intermediates leading to cyclopropane formation: (a) concerted transition state, (b) radical transition state, (c) diradical transition state, (d) C_3SMo metallacycle, and (e) C_3Mo metallacycle.

is cyclopropane, and not propene (the only other conceivable product) for several reasons. First, as will be demonstrated below, the formation of cyclopropane is enthalpically favorable by approximately 31 kcal/mol. Second, the mass spectrometric m/e 41:42 ratio of the product assigned as cyclopropane quantitatively agrees with the 41:42 ratio of an authentic cyclopropane sample, but not with that of propene. The ratio of the peak at 320 K assigned as propene does quantitatively agree with an authentic sample of propene. Finally, the 190 K product does not incorporate surface deuterium, while propene adsorbed on clean and sulfided Mo(110) does incorporate surface deuterium. The desorption temperature of propene adsorbed on clean and sulfided Mo(110) is 190–200 K. If the 190 K product were propene, it would probably leave the surface in a desorption-limited process, and would be expected to incorporate surface deuterium. Therefore, the chemical properties of the molecule produced at 190 K are not in agreement with the known chemical properties of propene on Mo(110). The 190 K product is thus attributed to formation of cyclopropane.

Because the reactions of trimethylene sulfide on Mo(110) are complicated, and because the heating rate range of our crystal manipulator is limited, we cannot perform kinetic studies of the cyclopropane formation reaction. Thus, it is impossible to accurately measure the activation energy and preexponential factor leading to cyclopropane formation. Speculation about the microscopic details of the cyclopropane formation mechanism is therefore difficult. Still, using energetic arguments of the type developed by Benson to deduce the mechanisms of organic reactions based on their kinetic parameters,³³ some conclusions about mechanistic pathways can be made. In Benson's method, the activation energy leading to a hypothetical *transition state* is estimated using the known thermodynamic properties of stable molecules, such as ring strain and bond energy. The estimated energies are then compared to the experimental activation energies, and the most likely transition state is inferred. We will discuss three general pathways for cyclopropane formation from trimethylene sulfide in the context of Benson's method.

The first pathway is a direct process involving C-S bond breaking and C-C bond making without formation of a genuine intermediate, and without oxidative addition of a surface metal atom to a S-C bond. Two possible transition states for this kind of a process are shown in Figure 7a,b. One of the transition states, shown in 7a, implies a concerted reaction pathway, and one, 7b, implies a nonconcerted pathway. In the concerted pathway, the two C-S bonds are breaking while the C-C bond is forming. Although the bond-breaking and -making processes in the concerted pathway are simultaneous, they do not necessarily occur at the same rate. The degree of synchronicity in bond making and breaking determines the "tightness" of the transition state, which to a large degree determines the entropy of activation leading to the transition state. Thus, the entropy of activation of a concerted transition state cannot be reliably estimated, but it is certainly between -20 and +20 eu. (The extreme values represent the approximate entropy changes of two particles changing to one, and one particle changing to two, respectively.) The method of Redhead can be used to calculate the activation energy of a unimolecular surface reaction if the entropy of ac-

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tivation and temperature of reaction are known.³⁴ We therefore calculate that at 190 K, the temperature of cyclopropane formation, the activation energy of cyclopropane from a concerted pathway must be between 7 and 15 kcal/mol. Whatever the entropy of activation for a concerted transition state, the activation energy must be quite low. A low activation energy is expected in the concerted process, however. Bonds are being simultaneously made and broken in the concerted transition state, and the weak metal-sulfur lone-pair bond is being exchanged for a strong metal-atomic sulfur bond. (The metal-sulfur lone-pair bond energy is estimated to be 20 kcal/mol,³⁵ while the bond energy of sulfur on Mo(110) has been measured to be 100 kcal/mol.³⁶) Moreover, the ring strain of the product and reactant molecules are separated by only +7 kcal/mol. Thus, a concerted cyclic transition state is consistent with our data.

The second transition state, shown in Figure 7b, implies a mechanism in which one C-S bond breaks before the other, to give a radical transition state (SCH₂CH₂CH₂·). The resulting radical could undergo ring closure and C-S bond breaking to form cyclopropane. The entropy of activation for formation of this radical is expected to be either nearly zero or slightly positive, on the order of 8–10 eu.³⁷ At 190 K, the calculated preexponential factors for a process with such an entropy range are between 10¹³ and 10¹⁵. The activation energy is therefore between 11 and 13 kcal/mol. It is impossible to estimate the enthalpy of activation of the process leading to the radical transition state, but an upper limit of 40 kcal/mol may be deduced, depending on the Mo-thiolate bond energy (see Appendix). Assuming a Mo-thiolate bond energy of 66 kcal/mol, the activation energy would be 13 kcal/mol. Thus, a monoradical transition state cannot be excluded on the basis of energetic grounds.

A final mechanism that does not involve oxidative addition of the metal to a C-S bond involves scission of both C-S bonds and formation of a 1,3-propyl diradical, as shown in Figure 7c. Cyclopropane formation during pyrolysis of the closely related molecule trimethylene 1,1-disulfoxide is known to occur by way of a 1,3-diradical transition state.³⁸ We estimate an entropy change of +20 eu for formation of a 1,3-diradical, based on the known entropy of activation for trimethylene 1,1-disulfoxide decomposition. This entropy of activation is consistent with the fact that in this mechanism two particles are created from one. The preexponential factor is therefore calculated to be 10¹⁷ at 190 K. An enthalpy of activation for cyclopropane formation of 15 kcal/mol is calculated assuming first-order kinetics and a preexponential of 10¹⁷ s⁻¹. However, the thermodynamically estimated enthalpy of activation is 50 kcal/mol (see Appendix). The fact that the activation energy for cyclopropane formation must be low due to its low temperature of formation is incompatible with the thermodynamically calculated activation energy. A diradical mechanism cannot be operative.

A second possible pathway leading to cyclopropane formation involves oxidative addition of molybdenum to one C-S bond. Such a pathway would lead to a C₃S₂Mo metallacycle. A possible representation of a C₃S₂Mo metallacycle is shown in Figure 7d. The metallacycle could then decompose intramolecularly to yield gaseous cyclopropane and surface sulfur. This five-membered metallacycle might exist as a genuine surface intermediate, or as a transition state. We are unaware of any previous identification of such a metallacycle, and so we cannot speculate on the possibility of its formation. The formation of a C₃S₂Mo metallacycle on the pathway toward cyclopropane formation seems unlikely, however. In general, five-membered metallacycles are subject to little thermodynamic ring strain.³⁹ Because the thermodynamic driving force for cyclopropane formation from trimethylene sulfide

with low activation energy is the release of trimethylene sulfide ring strain (vide infra), it is difficult to rationalize a mechanism in which the rate-limiting step is decomposition of an intermediate that is not itself thermodynamically strained. The fact that the less strained saturated cyclic sulfide, tetrahydrothiophene, does not produce cyclobutane⁶ is further evidence that a sulfur-containing metallacycle is an unlikely intermediate.

In a final mechanism, surface metal atoms could oxidatively add to both C-S bonds in a process that entirely excludes sulfur from the trimethylene sulfide ring. The resulting intermediate or transition state would then be a metallacyclobutane, schematically shown in Figure 7e. The four-membered metallacycle could then undergo ring contraction to yield gas-phase cyclopropane. Such processes are well known in the case of homogeneous Pt(II) metallacyclobutanes.⁴⁰ For instance, bis(trialkylphosphine)-3,3-dimethylplatinacyclobutanes thermally decompose to produce bis(trialkylphosphine)platinum(0) and 1,1-dimethylpropane.⁴¹ It is, however, difficult to imagine an energetically and entropically favorable pathway by which the surface metallacycle might be formed. In the decomposition mechanisms discussed above, the formation of a strong bond between molybdenum and atomic sulfur provides a strong thermodynamic driving force for decomposition to cyclopropane. If a metallacyclobutane were a reaction intermediate, there could be no such driving force. Furthermore, the enthalpies of activation of cyclopropane elimination from homogeneous complexes are on the order of 40 kcal/mol, greater than the activation energy available for a process that takes place at 190 K for any reasonable preexponential factor. This difference in activation energies does not prove that trimethylene sulfide does not decompose to cyclopropane by way of a metallacyclobutane. Many factors that contribute to the energy of the transition states in these transition metal complexes, such as steric interactions between the phosphine ligands, do not contribute to the activation energy of a surface reaction. Also, there may be significant differences in reactions on chromium group surfaces compared to those of nickel group metal complexes. Still, the difference in activation energies is substantial (approximately 25 kcal/mol), suggesting that a metallacyclobutane pathway is unlikely.

Of the three general cyclopropane formation pathways discussed above, the first, where no oxidative addition occurs, appears to be most plausible. These pathways require the fewest number of steps, and they are probably the most energetically reasonable. Energetic and entropic considerations suggest that the concerted pathway is accessible at 190 K, and that the monoradical pathway may be accessible. A diradical mechanism is almost certainly not involved in the production of cyclopropane. The two pathways that involve oxidative addition of C-S bonds and metallacycle formation cannot be excluded. Still, they are considerably more complicated, and they may not be energetically feasible.

Competing with formation of cyclopropane from trimethylene sulfide is ring opening of trimethylene sulfide to form the same adsorbed propyl thiolate formed by surface dissociation of 1-propanethiol. The microscopic details of the ring-opening reaction are of course unknown. We note, however, that the cyclopropane yield is insensitive to the surface hydrogen coverage. Thus, cyclopropane and the adsorbed thiolate cannot be formed from two competing fast reactions of the same transition state or intermediate if one of those reactions is a hydrogenation to the surface thiolate. The most logical mechanism consistent with this fact invokes two different transition states or intermediates. For instance, concerted ring contraction of trimethylene sulfide to cyclopropane might compete with ring opening to the monoradical discussed above, followed by fast hydrogenation of the radical to the thiolate.

The propyl thiolate from either trimethylene sulfide or 1-propanethiol selects between two reaction channels that lead to hydrocarbon formation, depending upon the surface hydrogen

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concentration. At low temperatures (below 350 K), the surface hydrogen concentration is high. Hydrogenation of the propyl thiolate at the C-S bond occurs, resulting in reaction-limited production of gas-phase propane. At approximately 350 K, desorption-limited evolution of hydrogen from the surface starts, depleting the surface hydrogen concentration. Hydrogenation of C-S bonds becomes statistically unlikely. Instead, selective dehydrogenation of the carbon located β to sulfur in the propyl thiolate occurs, resulting in production of propene. β -Dehydrogenation is the simplest mechanism by which the adsorbed thiolate can react to form propene. Dehydrogenation at any other carbon would require subsequent rearrangement of hydrogen along the hydrocarbon skeleton for propene evolution to occur. While the rates of the competitive hydrogenation and dehydrogenation pathways are controlled mostly by the surface hydrogen concentration, it is also true that in some parts of the temperature-programmed reaction spectrum, propane and propene evolve from the surface simultaneously. Therefore, the energetics for the two processes must be fairly closely matched.

We have discussed before a possible geometry of an alkyl thiolate on Mo(110), based on the known bonding of alkyl thiolates to Fe₃ clusters in discrete transition metal complexes. Briefly, sulfur bonds to the surface in a pseudo-three-fold position, on one side of one of the hour-glass troughs present on a bcc (110) surface. This geometry is important because it predicts that the steric requirements for both hydrogenation to propane and β -dehydrogenation to propene are not demanding. A more extensive discussion of the thiolate geometry is presented in previous work.⁶

The two hydrogen peaks in the temperature-programmed reaction spectra of trimethylene sulfide and 1-propanethiol are very similar to the hydrogen peaks seen in the temperature-programmed reaction spectrum of other sulfur-containing hydrocarbons on molybdenum surfaces. The β_1 peak is proposed to originate from a superposition of desorption- and reaction-limited states, with desorption-limited hydrogen accounting for the near edge of the β_1 peak, and reaction-limited hydrogen accounting for the far edge. This conclusion is based upon the hydrogen and deuterium coadsorption experiments, described above.

The β_2 -H₂ peak temperature is too high for it to result from the recombination of surface hydrogen atoms. We attribute it to the reaction-limited decomposition of a surface hydrocarbon fragment. The β_2 -dihydrogen peak is first detected just at the exposure at which hydrocarbon production begins. This fact suggests that the intermediate which decomposes to propene and propane also reacts to form the fragment which eventually decomposes to β_2 -dihydrogen. We therefore propose that a fraction of the propyl thiolate does not decompose to propane and propene. It instead decomposes, perhaps by dehydrogenation of a carbon atom not located β to sulfur, to give the reaction-limited hydrogen detected at the far edge of the β_2 peak and an irreversibly bound hydrocarbon fragment. The irreversibly bound fragment decomposes at 540 K (trimethylene sulfide) or 545 K (1-propanethiol) to β_2 -dihydrogen. The molecular geometry or stoichiometry of the irreversibly bound fragment is unknown. The relatively high decomposition temperature of the fragment which yields β_2 -dihydrogen is attributed to the presence of sulfur on the surface. An analogous peak is observed for thiophene, tetrahydrothiophene, and 1-butanethiol adsorbed on Mo(110), and for propene adsorbed on a presulfided surface.¹⁵ The fact that this decomposition peak is observed for a range of different molecules, with and without sulfur covalently bound to the adsorbate, suggests that the rate-limiting process is C-H bond cleavage in the presence of adsorbed atomic sulfur. The peak is not dependent on a heteroatom covalently bound to the adsorbed fragment. Spectroscopic studies, namely X-ray photoemission and high-resolution electron energy loss spectroscopy, are planned to characterize the fragment which decomposes to β_2 -dihydrogen.

At very high exposures, small amounts of 1-propanethiol reversibly desorb from Mo(110) between 175 and 200 K. As shown in Figure 5, desorption of 1-propanethiol does not occur unless the exposure is sufficiently high to virtually saturate all other reaction pathways. Thus, desorption of 1-propanethiol probably

Table V. Estimated Enthalpies (kcal/mol) of Desulfurization of Trimethylene Sulfide and Tetrahydrothiophene on Mo(110)^a

hydrocarbon produced	trimethylene sulfide	tetrahydrothiophene
cycloalkane	-31	-14
terminal alkene	-39	-21
<i>cis</i> -alkene		-23
<i>trans</i> -alkene		-24
alkane	-49	-31

^a The effect of the increased ring strain in trimethylene sulfide is manifested in an increased reaction exothermicity for all C₃ hydrocarbon products.

does not complete with another reaction, such as surface dissociation of the S-H bond. Reversibly chemisorbed 1-propanethiol is wholly molecular, as demonstrated by the lack of deuterium incorporation into the 1-propanethiol peak. The low desorption temperature suggests a weak interaction between 1-propanethiol and Mo(110), certainly much weaker than tetrahydrothiophene and Mo(110).⁶ The low temperature of 1-propanethiol desorption suggests that this peak does not originate from simple desorption from a chemisorbed state. The 1-propanethiol desorption peak may be due to desorption from a compressed monolayer layer with significant intermolecular repulsion. This explanation is consistent with the coverage dependence of the desorption temperature. Alternatively, the 1-propanethiol peak may be due to displacement of chemisorbed 1-propanethiol into the gas phase induced by a surface reaction such as S-H bond cleavage.

The proposed mechanism, summarized in Figure 6, is consistent with all data, including the surface deuterium incorporation results. The mechanism predicts that no deuterium should be incorporated into cyclopropane, as was experimentally observed. Moreover, propane from trimethylene sulfide is expected to have incorporated at most two surface deuterium atoms, while propane from 1-propanethiol should have incorporated only one deuterium. Propene from trimethylene sulfide should have one deuterium, but propene from 1-propanethiol should have no deuterium. Again, these predictions are in accord with experimental observation.

The selectivity for hydrogenation to propane vs. dehydrogenation to propene is expected to depend upon the coverage of atomic hydrogen, as is observed. If hydrogen is preadsorbed on Mo(110) to saturation, the propane/propene ratio from trimethylene sulfide increases from 0.4 to 0.8. The propane/propene ratio from 1-propanethiol is higher still, since the coverage of atomic hydrogen must necessarily be greater than or equal to the coverage of propyl thiolate. Thus, relatively more of the propyl thiolate is hydrogenated to propane if 1-propanethiol is the adsorbate, and the propane/propene ratio is 3.0. Preadsorbed hydrogen does not affect the yield of propene from 1-propanethiol, presumably because the surface hydrogen coverage is so great that pseudo-first-order kinetics are operative.

Although the reactions of saturated C₃S molecules are in some respects like the reactions of saturated C₄S molecules, they are also different. Trimethylene sulfide yields cyclopropane at the low temperature of 190 K, while tetrahydrothiophene does not decompose to cyclobutane. In addition, some tetrahydrothiophene reversibly binds to Mo(110); its desorption temperature is 310 K. No trimethylene sulfide desorption from Mo(110) is detected. These differences are attributed to the effects on free energy of activation of ring strain.

Ring-strain effects are to be expected to be important in controlling the surface reactivity of these molecules. In Table V are presented the estimated enthalpies of several hydrocarbon formation reactions on Mo(110).³⁵ The desulfurization reactions of trimethylene sulfide are uniformly 18 kcal/mol more exothermic than the analogous reactions of tetrahydrothiophene. This effect is almost entirely due to the enhanced ring strain in trimethylene sulfide, which is 19 kcal/mol, compared to a ring strain of 2 kcal/mol in tetrahydrothiophene. While overall thermodynamics obviously do not entirely control the reactivity of these molecules, they do suggest what reactions might be favorable. Certainly if a desulfurization reaction is favorable for tetrahydrothiophene,

it will be even more favorable for trimethylene sulfide. The additional 18 kcal/mol available to trimethylene sulfide might explain why 75% of adsorbed trimethylene sulfide decomposes to hydrocarbons, while only 25% of tetrahydrothiophene decomposes to hydrocarbons. Furthermore, cyclobutane formation from tetrahydrothiophene is calculated to be much less favorable than any of the hydrocarbon formation pathways that are observed. The fact that cyclopropane formation from trimethylene sulfide is more energetically favorable than even alkene formation from tetrahydrothiophene further confirms the assertion that cyclopropane is formed from trimethylene sulfide reaction at 190 K.

The real driving force of a reaction is of course not overall thermodynamics, but kinetics. However, the ring strain of trimethylene sulfide is expected to uniformly lower the activation energy barrier of all trimethylene sulfide reactions. For instance, opening of the heterocyclic ring to a thiolate should occur at a lower temperature for trimethylene sulfide than for tetrahydrothiophene because the transition state for ring opening must exhibit some degree of C-S bond breaking and ring-strain release. We postulated above that ring opening of trimethylene sulfide occurs at 190 K in a process competitive with cyclopropane formation. If that is true, then no molecularly chemisorbed trimethylene sulfide can be present on the surface above 275 K, the temperature at which the intensity of the cyclopropane formation peak drops to zero. In the case of tetrahydrothiophene, we proposed that butyl thiolate formation competed with tetrahydrothiophene desorption at 315 K. These data are consistent with our ring-strain analysis. No cyclobutane formation from tetrahydrothiophene is observed because all tetrahydrothiophene has reacted before the surface can provide enough thermal energy for the activation barrier leading to cyclobutane formation to be surmounted. In contrast, no molecular desorption of trimethylene sulfide is detected because no trimethylene sulfide remains on the surface at 315 K, the approximate desorption temperature of trimethylene sulfide if it were on the surface, assuming that the adsorption energy for trimethylene sulfide and tetrahydrothiophene are approximately the same.

We have rationalized our product formation data on the basis of ring-strain analysis. There is one other difference between the reactions of C₃ and C₄ molecules. Propane and propene formation from trimethylene sulfide and 1-propanethiol occur at a lower temperature than butane and butene formation from tetrahydrothiophene and 1-butanethiol. The temperature differences are not large, about 30 K. These differences are attributed to the effects of different carbon, sulfur, and hydrogen coverages on the energetics of the pathways leading to hydrocarbon production. If 1-propanethiol and 1-butanethiol are coadsorbed on Mo(110), then the C₃ hydrocarbons evolve at the same temperature as the C₄ hydrocarbons. Therefore, the temperature differences do not reflect differences in the intermediates, but in the surface composition.

Conclusions

Trimethylene sulfide and 1-propanethiol react to form dihydrogen, propane, and propene on Mo(110). Trimethylene sulfide also reacts by a low-energy pathway to form cyclopropane. A very small amount of 1-propanethiol reversibly chemisorbs on Mo(110). Cyclopropane is proposed to be formed by an intramolecular pathway, through either a concerted or monoradical transition state. The similarity in the dihydrogen, propane, and propene peaks from the two molecules suggests that they decompose by way of the same intermediate. The intermediate is proposed to be a surface propyl thiolate. Hydrogenation of a C-S bond in trimethylene sulfide and simple S-H bond scission in 1-propanethiol yield the surface thiolate. The propyl thiolate undergoes hydrogenation to propane or dehydrogenation to propene, depending on the surface hydrogen concentration. The reaction of trimethylene sulfide and tetrahydrothiophene were compared, and the differences in their reactions was attributed mostly to the greater ring strain in trimethylene sulfide.

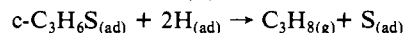
Acknowledgment. This work was supported by the Department of Energy, Basic Energy Sciences, Grant No. DE-FG02-

84ER13289. J.T.R. thanks the DuPont Corp. for a tuition fellowship (1984-85).

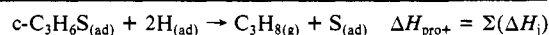
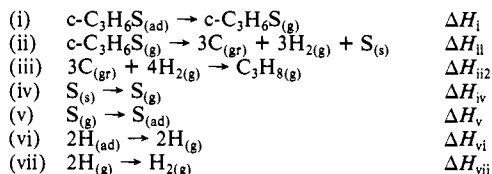
Appendix: Calculation of Enthalpies of Trimethylene Sulfide and 1-Propanethiol Desulfurization on Mo(110)

The estimate of thermodynamic values of surface reactions is not an easy task. Very little reliable data concerning such fundamental quantities as heats of atomic adsorption on transition metal surfaces are available. Nevertheless, we were interested in estimating the enthalpies of trimethylene sulfide and tetrahydrothiophene desulfurization on Mo(110). Of particular interest to us was whether enhanced ring strain in trimethylene sulfide could rationally account for our observation of cyclopropane formation. The following analysis demonstrates our method of calculating these enthalpy changes. Because there are so few methods of directly measuring surface thermodynamic quantities, we were forced to make a number of assumptions which will be discussed below. These assumptions taken together introduce substantial systematic error to the values we calculate for enthalpy change (estimated to be ± 10 kcal/mol). However, in most cases the same assumptions were made for every reaction. Therefore, the difference in enthalpy change between any two desulfurization reactions is probably quite accurate.

All enthalpies of reaction were calculated using Hesse's law. As an example, we will consider the desulfurization of adsorbed trimethylene sulfide (c-C₃H₆S_(ad)) to gaseous propane (C₃H_{8(g)}):



The heat of desulfurization to propane, ΔH_{prop} , may be estimated by summing the enthalpy changes of an appropriate set of reactions i-vii. The heat of desorption of trimethylene sulfide, ΔH_{i} , may



be estimated by considering the case of tetrahydrothiophene, which is known to desorb from Mo(110) at 310 K.⁶ Since tetrahydrothiophene and trimethylene sulfide are structurally and electronically very similar, trimethylene sulfide presumably bonds to Mo(110) with approximately the same energy as tetrahydrothiophene. In solution, trimethylene sulfide has been determined to be slightly less basic than tetrahydrothiophene.⁴² If, as we propose, tetrahydrothiophene and trimethylene sulfide bond to Mo(110) as Lewis bases, then the adsorption energy of trimethylene sulfide is probably smaller than the adsorption energy of tetrahydrothiophene. However, even if the solution-phase basicity trend applies to the case of surface bonding, the estimate will not be more than 2 kcal/mol in error. Redhead's method can be used to estimate the activation energy of desorption. The adsorption of tetrahydrothiophene is assumed to be nonactivated, so that the desorption energy is equal to the activation energy of desorption. The assumption that the adsorption process is nonactivated results in a high estimate of the desorption energy, but again the error introduced by this assumption is certainly quite small. Using Redhead's model, a heating rate of 15 K/s, and assuming a preexponential factor of 10¹³, we estimate the desorption energy to be 18 kcal/mol. The heat of adsorption is assumed not to change greatly with surface temperature.

The quantities ΔH_{ii} and ΔH_{iii} are the negative heat of formation of trimethylene sulfide and the heat of formation of propene, respectively. Heats of formation at 298 K are easily calculated using the extremely accurate group additivity method of Benson.⁴³

(42) Dittmer, D. C.; Sedergran, T. C. *Heterocycles*, Part 3; Hassner, A., Ed.; Wiley: New York, 1985; Vol. 42, p 441.

(43) Benson, F. W.; Cruikshank, F. R.; Golden, D. M.; Haugen, G. R.; ONeal, H. E.; Rodgers, A. S.; Shaw, R.; Walsh, R. *Chem. Rev.* 1969, 69, 279-324.

The enthalpies of formation were estimated because the group additivity formalism gives explicit thermodynamic values for such concepts as ring strain and steric interactions. The temperature range that concerns us, 190 to 350 K, is sufficiently narrow and close to standard-state temperature that the temperature dependence of enthalpy should not introduce a large error. Using Benson's method we calculate that the heat of formation of trimethylene sulfide, $-\Delta H_{\text{f}}^{\circ}$, is -14.6 kcal/mol. Ring-strain accounts for $+19.4$ kcal/mol of the heat of formation. The heat of formation of propane is -25.1 kcal/mol.

The heat of vaporization solid sulfur to monoatomic sulfur, ΔH_{iv} , and the heat of atomization of gaseous hydrogen, $-\Delta H_{\text{vii}}$, are well-known quantities. ΔH_{iv} is 53.3 kcal/mol at 298 K and ΔH_{vii} is -104.2 kcal/mol.⁴⁴

The heat of atomic sulfur adsorption on Mo(110), ΔH_{v} , has been determined by other workers to be 100 kcal/mol for one-half of a monolayer of sulfur.³⁶ This estimate is in reasonable agreement with the Mo-S bond energy in solid MoS₂ (81 kcal/mol) and the heat of adsorption of S on Ru(100) (105 kcal/mol at low coverages).⁴⁵ The value 100 kcal/mol is also in agreement with our observation that sulfur desorbs from Mo(110) at temperatures greater than 1500 K, corresponding to an activation energy of desorption greater than 100 kcal/mol.

The heat of atomic hydrogen adsorption on Mo(110), $-\Delta H_{\text{vi}}$, is estimated to be -62 kcal/mol.⁴⁶ This value is in good agreement with our estimate of $\Delta H_{\text{vi}} = 60$ kcal/mol, assuming nonactivated dissociative hydrogen adsorption, and using Redhead's model.

Using these seven values, we estimate that the enthalpy of trimethylene sulfide desulfurization to propane is -49 kcal/mol, suggesting that desulfurization is a very favorable process. All other values listed in Table V were calculated in an exactly analogous fashion.

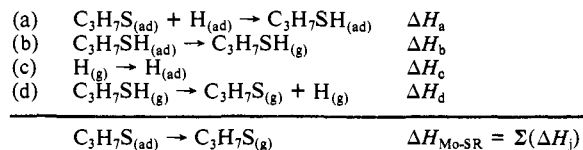
The activation energies of the ring-opening reactions of trimethylene sulfide are estimated using a method similar to that described above. The energies of the bonds broken in the process leading to the transition state are added, the energies of the bonds

formed are subtracted, and ring-strain effects are added. For instance, consider the ring opening of trimethylene sulfide on Mo(110) to a surface thiolate radical (Mo-SCH₂CH₂CH₂). The energy for this process is equal to:

$$D(\text{C-S}) + D(\text{Mo-tms}) - D(\text{Mo-SR}) - S(\text{tms})$$

where D represents a bond energy and $S(\text{tms})$ represents the ring strain of trimethylene sulfide. The values of $D(\text{C-S})$ and $S(\text{tms})$ are well known; they are 75^{30} and 19 kcal/mol,⁴³ respectively. The strength of a Mo-trimethylene sulfide bond, $D(\text{Mo-tms})$, is just the heat of adsorption of trimethylene sulfide, calculated above to be 18 kcal/mol.

The bond energy of an alkyl thiolate, $D(\text{Mo-SR})$, can only be assigned a lower limit. This limit is calculated using another thermodynamic cycle: The value ΔH_{a} represents the negative



heat of dissociation of 1-propanethiol on Mo(110). The heat of dissociation of 1-propanethiol is unknown, but the temperature at which it occurs, based upon the temperature at which propane appears in a temperature-programmed reaction, must be less than 200 K. The heat of dissociation must therefore be less than or equal to the activation energy for a first-order process that occurs at 200 K. Using Redhead's equation, an activation energy of 12 kcal/mol is calculated. This, then, is the upper bound on ΔH_{a} . The quantities ΔH_{b} and ΔH_{c} were calculated above. They are 18 and 62 kcal/mol, respectively. The gas-phase S-H bond energy, ΔH_{d} , is known to be 88 kcal/mol. The strength of the Mo-thiolate bond is the sum of these four enthalpies of reaction. Therefore, $D_{\text{Mo-thiolate}}$ must be greater than or equal to 32 kcal/mol.

Because the bond energy of a thiolate can only be assigned a lower limit, the activation energy for ring opening to a thiolate radical can only be assigned an upper limit. Adding the appropriate values for $D(\text{C-S})$, $D(\text{Mo-tms})$, $D(\text{Mo-SR})$, and S , we find that the energy of ring opening to a radical transition state is less than or equal to 42 kcal/mol.

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