

Ion and Radical Rearrangements as a Probe of the Mechanism of a Surface Reaction: The Desulfurization of Cyclopropylmethanethiol and 3-Butene-1-thiol on Mo(110)

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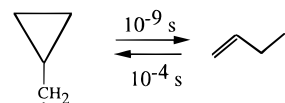
Abstract: Rearrangement reactions were used to probe the transient intermediates in thiol desulfurization induced by Mo(110) by studying cyclopropylmethanethiol and 3-butene-1-thiol. Thiolate intermediates were identified in both cases using vibrational spectroscopy, which indicates facile S–H bond scission on Mo(110). Heterolytic C–S bond scission, leading to a cationic intermediate, is excluded based on the lack of rearrangement products in the reactions of 3-butene-1-thiolate and the absence of cyclobutane or cyclobutene in the reaction of cyclopropylmethyl thiolate on Mo(110). Hydrogenolysis without rearrangement is the primary pathway for both thiols investigated. The lack of rearrangement in the 3-butene-1-thiolate indicates that C–S bond scission and C–H bond formation occur nearly simultaneously. Evidence for the radical pathway is obtained from the production of 1,3-butadiene formed via the rearrangement of cyclopropylmethyl group following C–S bond scission in the cyclopropylmethyl thiolate and by related studies of cyclopropylmethyl bromide. The investigation of the cyclopropylmethyl bromide also demonstrates that trapping of the cyclopropylmethyl radical is favored over selective β -dehydrogenation. This is the first study in which radical rearrangements have been used to obtain detailed information about the nature of extremely short-lived reactions in a surface process.

Introduction

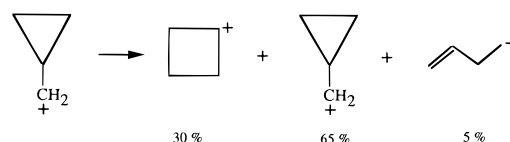
The study of reactions of sulfur-containing molecules on transition metal surfaces has been the subject of intense investigation due to their importance in industrial hydrodesulfurization processes. We have studied a range of different thiols on Mo(110) and have proposed a general mechanism for their reaction. The S–H bond of all thiols studied cleaves upon adsorption at 120 K to form the corresponding thiolate, which remains intact on the surface up to the temperature required for C–S bond scission and hydrocarbon elimination. In the reaction of thiolates on Mo(110), alkane formation competes with alkene and nonselective decomposition.^{1,2} The selectivity for hydrocarbon production increases over nonselective decomposition at high thiolate coverages. The same mechanism was consistent with data obtained for a variety of different alkyl thiolates.^{1,3–8}

The temperature required for C–S bond hydrogenolysis on Mo(110) depends strongly upon the alkyl group and generally correlates with the gas-phase, homolytic C–S bond strength of the thiols, suggesting that an alkyl radical is eliminated first followed by hydrogenation to form an alkane or β -dehydrogenation leading to the corresponding alkene. For example, 2-methyl-2-propyl thiolate reacts more rapidly than primary thiolates, such as ethanethiolate.^{4,5} The strength of 2-methyl-

Scheme 1



Scheme 2



2-propyl thiol C–S bond is 68.4 kcal/mol, with a heat of formation for the radical of 7.6 kcal/mol, compared to a C–S bond strength of 72.2 kcal/mol for ethanethiol and a heat of formation of 25.9 kcal/mol for the radical.⁵ These data indicate a high degree of C–S bond breaking, but radical-like, cationic, and concerted mechanisms are all possible. Anionic mechanisms are unlikely because of the relatively high electronegativity of sulfur which renders electron transfer to the alkyl unfavorable.

Herein, the reactions of cyclopropylmethanethiol are used to probe for radical and cationic intermediates by exploiting the rapid isomerizations of the cyclopropylmethyl radical and cation (Schemes 1 and 2). Although the time scales for rearrangement in the vicinity of the surface might be different than in the gas phase, they are still expected to be rapid based on recent reports of rearrangements in mixed Mo–Co complexes.³⁷ Accordingly, carbon–sulfur bond homolysis to a radical species is expected to lead to rapid conversion (10^{-9} s) to a 3-buten-1-yl radical based on known gas-phase chemistry (Scheme 1).^{9,10} The 3-buten-1-yl radical could then hydrogenate to form 1-butene,

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dehydrogenate to 1,3-butadiene, or trap on the surface and nonselectively decompose. Alternatively, heterolytic C–S bond cleavage would yield the cyclopropylmethyl cation, which is in equilibrium with both the 3-buten-1-yl cation and cyclobutyl cation in the gas phase (Scheme 2).^{11–13} Hydrogenation following heterolytic C–S bond cleavage would yield a mixture of cyclobutane, methylcyclopropane, and 1-butene. Dehydrogenation would yield a mixture of cyclobutene and 1,3-butadiene. The reactions of 3-butene-1-thiol were studied as an additional probe for a cationic mechanism. In this case, the 3-buten-1-yl cation would rearrange to a mixture of cyclopropylmethyl, cyclobutyl, and 3-buten-1-yl cation (Scheme 2).¹⁴ Again, hydrogenation would yield a mixture of cyclobutane, methylcyclopropane, and 1-butene, and dehydrogenation would yield a mixture of cyclobutene and 1,3-butadiene. If C–H bonds form more rapidly than rearrangement after sulfur elimination, no rearrangement is expected, and only methylcyclopropane would be produced. Finally, C–S bond scission forming a surface alkyl intermediate could follow one of three pathways: (1) hydrogen addition, yielding methylcyclopropane; (2) β -dehydrogenation to 1,3-butadiene; or (3) nonselective decomposition to surface carbon, sulfur, and $\text{H}_2(\text{gas})$. The reactions of ethyl chloride and cyclopropylmethyl bromide, which undergo carbon halogen bond cleavage at low temperatures to produce stable alkyl intermediates, are used to probe for these pathways.

Experimental Section

The experiments were performed in three ultrahigh vacuum chambers described previously with base pressures of $\leq 2 \times 10^{-10}$ Torr.^{15–17} All three chambers were equipped with a UTI quadrupole mass spectrometer, low energy electron diffraction (LEED) optics, and an Auger spectrometer with cylindrical mirror analyzer. The high resolution electron energy loss spectrometer (LK technologies, model LK2000) was operated at a primary beam energy of 3 eV, with a spectral resolution of 55–80 cm^{-1} . The variation in the resolution was due to the different reflectivities of the condensed and monolayer thiol phases that were studied. The infrared spectra were collected using a single beam, clean air purged Fourier transform infrared spectrometer (Nicolet, Series 800) and averaged over 800 scans using an MCT detector at 4 cm^{-1} resolution; the scan time being approximately 5 min. Sample spectra were ratioed against a background taken immediately after the sample scan by flashing the crystal to 900 K. The background scan was initiated after the crystal temperature had returned to ≈ 100 K.

The Mo(110) crystal (Metal Crystals Ltd.) could be cooled to 100 K, heated to 900 K radiatively, or heated to 2300 K by electron bombardment. The Mo(110) surface was cleaned before each experiment by oxidation at 1200 K in 1×10^{-9} Torr of O_2 for 5 min. The crystal temperature was allowed to return to ≈ 200 K and subsequently flashed to 2300 K for 30 s to remove residual oxygen. No surface carbon or oxygen were detected in the Auger electron spectra of the surface recorded prior to cyclopropylmethanethiol adsorption. A sharp (1×1) low energy diffraction pattern was also observed.

3-Butene-1-thiol^{18,19} and methylcyclopropane²⁰ were synthesized using established methodology. The cyclopropylmethanethiol was purchased from Lancaster.²¹ The compounds were characterized by mass spectrometry and nuclear magnetic resonance. Cyclopropylmethyl bromide was purchased from Aldrich and was characterized by mass spectroscopy.

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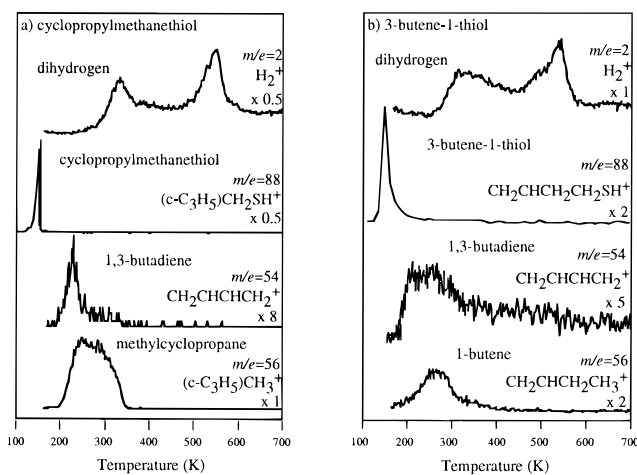


Figure 1. Temperature-programmed reaction data following condensation of multilayers of (a) cyclopropylmethanethiol and (b) 3-butene-1-thiol on initially clean Mo(110). The spectra for ions representative of methylcyclopropane, $m/e = 56$; 1,3-butadiene, $m/e = 54$; 1-butene, $m/e = 56$; cyclopropylmethanethiol, $m/e = 88$; 3-butene-1-thiol, $m/e = 88$; and dihydrogen, $m/e = 2$ are shown. The heating rate was nearly constant at 4 K/s in the range shown.

The crystal was positioned approximately 2 mm from the aperture (3 mm) of the mass spectrometer shield during the collection of temperature-programmed reaction data. The crystal was biased at -65 eV during temperature-programmed reaction to minimize reactions induced by electrons generated by the quadrupole mass spectrometer. The mass spectrometer was computer interfaced and the data were collected with a program, which allowed collection of up to 10 separate ion intensity profiles during a single experiment. The heating rate was constant with $dT/dt = 4$ K/s between 110 and 650 K.

Results

Temperature Programmed Reaction Spectroscopy. Two hydrocarbon products, methylcyclopropane and 1,3-butadiene, are produced during temperature-programmed reaction of a saturation coverage of cyclopropylmethanethiol (Figure 1a). The only other gaseous product detected in a comprehensive search for products in the range of 2–110 amu was gaseous dihydrogen. Condensed layers of cyclopropylmethanethiol sublime from Mo(110) in a sharp peak at 150 K (Figure 1a, $m/e = 88$). This peak increases indefinitely with continued cyclopropylmethanethiol exposure, as expected. All of the products are observed at saturation coverage and are identified by quantitative analysis of mass spectrometer data.

Methylcyclopropane is the major gas phase hydrocarbon product and evolves between 200 and 350 K (Figure 1a, $m/e = 56$). Identification of methylcyclopropane was made by comparison of the mass fragmentation patterns of the product and an authentic sample of methylcyclopropane (Table 1). Formation of 1,3-butadiene is a minor pathway (Figure 1a, $m/e = 54$). 1,3-Butadiene evolves at 240 K and was identified by the mass 54 signal, which is significantly greater than measured for methylcyclopropane fragmentation. The methylcyclopropane fragmentation pattern was subtracted from the pattern at 240 K. The resulting fragmentation pattern compares favorably

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(19) ^1H NMR (CDCl_3 , 500 MHz) δ 5.81 (m, 1H), 5.06 (m, 2H), 2.74 (t, $J = 7$ Hz, 2H), 2.43 (m, 2H). The α hydrogen at δ 2.74 appeared as a triplet, rather than a quartet, and the S–H proton (typically at δ 1.2–1.4) was absent due to exchange of the latter with water.

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(21) ^1H NMR (CDCl_3 , 500 MHz) δ 2.43 (t, $J = 7$ Hz, 2H), 1.43 (t, $J = 7$ Hz, 1H), 0.97–1.10 (m, 1H), 0.49–0.60 (m, 2H), 0.13–0.28 (m, 2H).

Table 1

Mass Fragmentation Patterns of Authentic Samples									
	56	55	54	53	41	39	29	28	27
methylcyclopropane	45	33	2	10	100	60	45	43	50
1-butene	20	8		3	100	55	23	80	55
1,3-butadiene			40	30		100	2	20	84
Mass Fragmentation of Products									
	56	55	54	53	41	39	29	28	27
products from the reaction of cyclopropylmethanethiol									
methylcyclopropane ^a	40	20	3	10	100	70	35	50	70
1,3-butadiene ^b			50			100			85
products from the reaction of 3-butene-1-thiol									
1-butene + 1,3-butadiene ^c	24	11	15	8	100	80	30	80	70
1-butene ^d	24	11			100	50	30	75	45
1,3-butadiene ^e			51			100			72

^a 1,3-Butadiene formation from the reaction of cyclopropylmethyl thiolate maximizes at 240 K and is minimal at 300 K. There is no need to correct the fragmentation pattern for the 1,3-butadiene contribution. ^b The 1,3-butadiene fragmentation pattern was corrected for methylcyclopropane. Formation of 1,3-butadiene is a minor product pathway from the reaction of cyclopropylmethyl thiolate and consequently some of the fragment intensities are too low to be reliably compared. ^c Combined fragmentation pattern for 1,3-butadiene and 1-butene from the reaction of 3-butene-1-thiol. ^d The 1-butene fragmentation was corrected for 1,3-butadiene fragmentation. ^e The 1,3-butadiene fragmentation pattern was corrected for 1-butene. Formation of 1,3-butadiene is a minor product pathway from the reaction 3-butene-1-thiol, and consequently some of the fragment intensities are too low to be reliably compared.

to that measured for the most intense masses of an authentic 1,3-butadiene sample in our system (Table 1).²²

The identification of methylcyclopropane as the majority product was confirmed by trapping the reaction products on a second Mo(110) substrate and subsequently characterizing them by mass spectrometry and infrared spectroscopy.²³ The trapped methylcyclopropane desorbed at 150 K and was identified by comparison of the fragmentation pattern to that for authentic methylcyclopropane (Table 1).²⁴ Comparison of the 2700–3100 cm⁻¹ and the 900–1450 cm⁻¹ regions of the infrared spectra of the trapped products and methylcyclopropane confirms that methylcyclopropane is the predominant product of cyclopropylmethyl thiolate reaction (Figure 2, Table 2). The infrared spectrum of the trapped product corresponds well to literature values for condensed cyclopropane,²⁵ cyclopropylmethyl thiolate adsorbed on Mo(110), condensed cyclopropylmethyl bromide and condensed cyclopropylmethanethiol, all of which have similar molecular structures (Figure 2).²⁶ The peaks at 3058 and 3008 cm⁻¹ are not consistent with either adsorbed 3-buten-1-yl species or 3-butene-1-thiol based on the comparison with infrared data for 1-butene on Mo(110) (Figure 2, Table 2). Infrared data for 3-butene-1-thiol and methylcyclopropane were not available for comparison.

Dihydrogen evolves at 340 and 550 K (Figure 1a, *m/e* = 2). The low-temperature dihydrogen is attributed mainly to recombination of surface hydrogen, whereas the high-temperature dihydrogen is due to the nonselective decomposition of a surface

(22) Because 1,3-butadiene formation is a minor pathway, some of the butadiene masses have intensities, which are too low to be reliably compared to the authentic sample.

(23) Weldon, M. K.; Friend, C. M. *Rev. Sci. Instrum.* **1995**, *66*(11), 5192.

(24) The fragmentation pattern of the desorbing product is the same as authentic methylcyclopropane. Butadiene is not expected to contribute significantly to the peak even if trapped, because of its low yield.

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(26) The contribution of any trapped butadiene is minimal in these experiments based on the fact that no butadiene is detected in subsequent temperature-programmed desorption of the trapped product.

intermediate containing intact C–H bonds, because of the extremely high temperature of dihydrogen evolution.

The saturation coverage of cyclopropylmethyl thiolate is estimated to be 0.25 ± 0.01 monolayers, based on Auger electron data. Since no sulfur-containing products leave the surface, the amount of sulfur on the surface following temperature-programmed reaction to 750 K is equal to the amount of thiol that reacts. Accordingly, the S(LMM) Auger electron intensity measured after heating condensed cyclopropylmethanethiol to 750 K was compared to the intensity measured for a 0.35 monolayer sulfur overlayer,⁷ in order to establish the saturation coverage. The saturation coverage of cyclopropylmethanethiol on Mo(110) is similar to the saturation coverage observed for a number of other thiols studied, e.g., butanethiol.^{27,28} Residual carbon was also detected by Auger electron spectroscopy following temperature-programmed reaction to 750 K. The carbon Auger signal, which is a measure of the amount of nonselective decomposition, was also similar to the amount of residual carbon observed for butanethiol.²⁷

The distribution of products evolved during the temperature-programmed reaction of cyclopropylmethanethiol on initially clean Mo(110) depends on the cyclopropylmethanethiol exposure. At the lowest coverages studied, $\theta \leq 0.1$ monolayers of thiolate, dihydrogen is the only product evolving in a broad peak centered at 410 K. At intermediate coverages, $0.1 \leq \theta \leq 0.2$ monolayers, methylcyclopropane is the sole detectable hydrocarbon and is evolved near 300 K. Dihydrogen is also observed at 330, 375, and 530 K. 1,3-Butadiene is first detected for a coverage of 0.22 monolayers, 88% of saturation.

The presence of either adsorbed deuterium or hydrogen alters the product distribution for cyclopropylmethanethiol and decreases the saturation coverage. When a saturation coverage of deuterium or hydrogen is adsorbed on Mo(110) prior to cyclopropylmethanethiol exposure, the maximum amount of thiolate formed is approximately 0.2 monolayers compared to 0.25 monolayers for the clean surface. Methylcyclopropane at 270 K is the only hydrocarbon product evolving from the surface, and only one deuterium is incorporated into methylcyclopropane when deuterium is preadsorbed. 1,3-Butadiene is not observed when hydrogen or deuterium is adsorbed first. Furthermore, the integrated yield of high-temperature dihydrogen is reduced by approximately two-thirds when hydrogen is first adsorbed. This suggests that surface hydrogen abates C–H bond scission. A comparison between the amount of methylcyclopropane evolving from the clean and hydrogen precovered surfaces reveals that the fraction of the thiolate that forms methylcyclopropane increases on the hydrogen precovered surface, supporting the contention that dehydrogenation is inhibited by hydrogen.

1-Butene and 1,3-butadiene are produced during temperature-programmed reaction of a saturation coverage of 3-butene-1-thiol on Mo(110) (Figure 1b). The only other gaseous product detected in a comprehensive search for products in the range of 2–110 amu was gaseous dihydrogen. Condensed layers of 3-butene-1-thiol sublime from Mo(110) in a sharp peak at 150 K (Figure 1b, *m/e* = 88). All products are observed at saturation coverage and identified by quantitative analysis of the mass spectrometer data.

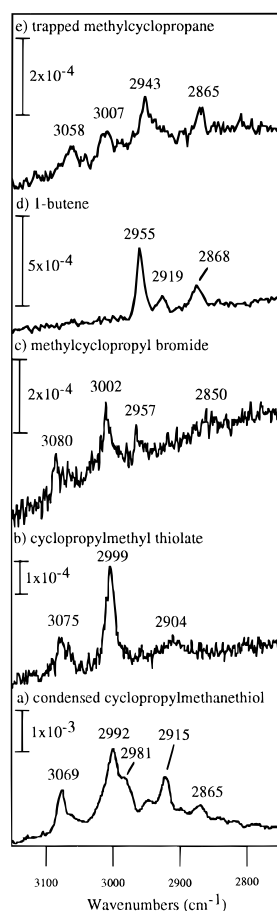
1-Butene is the major product produced during temperature-programmed reaction of a saturation coverage of 3-butene-1-thiol on Mo(110) (Figure 1b, *m/e* = 56). 1-Butene evolves over the temperature range of 200–400 K and was identified by

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Table 2. Vibrational Assignments for Cyclopropylmethanethiol and Cyclopropylmethyl Thiolate on Mo(110)

assignments	(C ₃ H ₅)CH ₂ SH		(C ₃ H ₅)CH ₂ S-		(C ₃ H ₅)CH ₂ Br	trapped product	C ₃ H ₆ ²⁵
	EELS	IR	EELS	IR	IR	IR	IR
$\nu(\text{C-H})$	2980	3069	2990	3075	3080	3058	3103
		2992		2999	3002	3007	3028
		2981		2904	2957	2943	
		2915			2850	2865	
		2865					
$\nu(\text{S-H})$	2545	2530					
CH ₂ scissor	1445	1422	1430	1428	1423		1441
CH ₂ wag, ring breathing	1230	1304	1200	1195	1223	1189	1188
		1256					
CH ₂ twist, ring deformation	1090	1048	1010	1012	1017		1028
		1019					
CH ₂ rock, ring deformation	830	938	830	958	958		905
$\nu(\text{C-S})$			590				
$\nu(\text{CCS}), \nu(\text{Mo-S})$	400		400				

**Figure 2.** Reflection infrared spectra of a) cyclopropylmethanethiol at 100 K; (b) cyclopropylmethyl thiolate; (c) cyclopropylmethyl bromide at 120 K; (d) 1-butene; and (e) trapped methylcyclopropane.

comparison to the mass fragmentation pattern obtained for an authentic sample of 1-butene in our system (Figure 1b, $m/e = 56$, and Table 1). A small amount of 1,3-butadiene is evolved over the temperature range of 200–350 K and was identified by the observation of mass 54 with significantly greater intensity than expected for 1-butene cracking (Figure 1b, $m/e = 54$). The 1,3-butadiene fragmentation pattern was subtracted from the combined fragmentation pattern for 1,3-butadiene and 1-butene at 300 K and the residual pattern compares favorably to that measured for 1-butene in our system (Table 1).²² Importantly, while other isomers of butene could also account for the fragmentation pattern of the product, it is *not* consistent with the formation of methylcyclopropane based on the $m/e = 56$: $m/e = 41$ ratio (Table 1).

Dihydrogen evolves at 330 and 550 K during the temperature-programmed reaction of 3-butene-1-thiol (Figure 1b, $m/e = 2$). The low-temperature dihydrogen is attributed to the recombination of surface hydrogens and the high-temperature peak to the nonselective decomposition of a surface intermediate containing intact C–H bonds, as before. Nonselective decomposition affording atomic sulfur and carbon and gaseous dihydrogen is a competing process.

Studies of cyclopropylmethyl bromide were undertaken to test the reactions of a radical species produced in the vicinity of the surface. Low temperature C–Br bond scission and hydrogenation results in methylcyclopropane at 130 K from clean Mo(110), based on the low temperature evolution of methylcyclopropane. No gaseous hydrocarbon evolution is observed above 200 K during the temperature-programmed reaction of cyclopropylmethyl bromide from clean and sulfur-covered Mo(110). Only dihydrogen and bromine evolve at temperatures above 300 K. 1,3-Butadiene is produced over a temperature range of 440–575 K, during temperature-programmed reaction of a saturation coverage of cyclopropylmethyl bromide on oxygen-covered Mo(110). The only other gaseous products detected in a comprehensive search for products in the range of 2–110 amu from oxygen-covered Mo(110) were gaseous dihydrogen and bromine. All products are observed at saturation coverage and identified by quantitative analysis of mass spectrometer data.

Vibrational Spectroscopy. Both high resolution electron energy loss and infrared reflection data indicate that the S–H bond in both cyclopropylmethanethiol and 3-butene-1-thiol is broken below 200 K, yielding the corresponding thiolates. Specifically, the $\nu(\text{S-H})$ mode observed at 2545 cm^{-1} in the electron energy loss spectrum of the condensed thiols is absent after heating to 200 K (Figure 3, Tables 2 and 3).²⁹ Similarly, the S–H stretch is observed in the infrared spectrum of condensed cyclopropylmethanethiol but not after heating to 200 K (data not shown).^{30,31} In all other respects, the electron energy

(29) The observed $\nu(\text{S-H})$ values for the condensed cyclopropylmethanethiol and 3-butene-1-thiol spectra are in good agreement with previous thiol studies.

(30) Orientation effects could, in principle, make the $\nu(\text{S-H})$ dipole forbidden and thus not observable in the IR. No other modes were observed in the IR.

(31) Infrared data were not obtained for 3-butene-1-thiol because there was insufficient sample available.

(32) The small feature at $\approx 1680 \text{ cm}^{-1}$ in both the condensed cyclopropylmethanethiol and cyclopropylmethyl thiolate spectra is attributed to a combination loss due to the $\delta(\text{CH}_2)$ mode at 1440 cm^{-1} and the $\nu(\text{CH}_3)$ mode at 240 cm^{-1} . The mode at 240 cm^{-1} is not resolved in our experiment, because it is obscured by the elastic peak. This relatively strong combination mode has been observed previously in IR and Raman spectra of gas and liquid phase substituted methyl cyclopropanes.

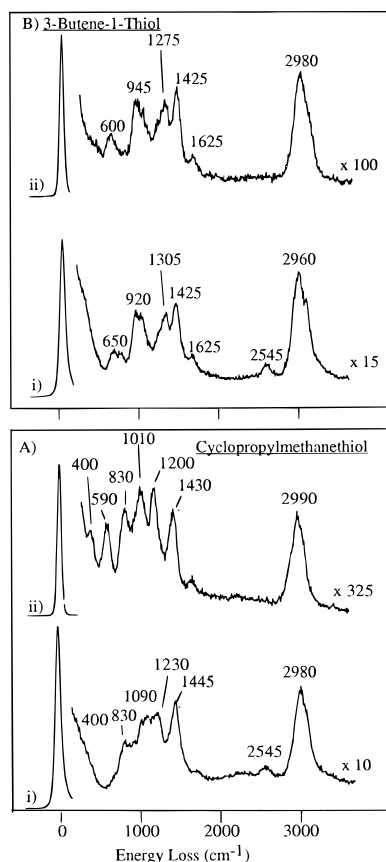


Figure 3. High resolution electron energy loss spectra of (a) condensed cyclopropylmethanethiol and (b) 3-butene-1-thiol at (i) 100 K and (ii) annealed to 200 K.

Table 3. Vibrational Assignments for 3-Butene-1-Thiol

assignment	C ₄ H ₇ SH EELS	C ₄ H ₇ S- EELS	C ₄ H ₈ 23 IR
$\nu(\text{C-H})$	2960	2980	2955 2919 2868
$\nu(\text{S-H})$	2545		
$\nu(\text{C=C})$	1625	1625	
CH ₂ scissors	1425	1425	1452
CH ₂ wag	1305	1275	
CH ₂ rock	920	945	
$\nu(\text{C-S}), \nu(\text{Mo-S})$	650	600	

loss spectra obtained after heating to 200 K are very similar to the condensed thiols (Figure 3, Tables 2 and 3), indicating that the hydrocarbon framework in the thiols is preserved upon S-H bond cleavage.³²

The C-H stretch region of the infrared spectrum of cyclopropylmethyl thiolate likewise indicates that the ring structure is preserved for the majority species on the surface (Figure 2). In particular, the peak at 3075 cm⁻¹ is *not* consistent with an adsorbed 3-buten-1-yl species based on the comparison with infrared data for 1-butene on Mo(110) but is consistent with cyclopropylmethyl thiolate and condensed layers of cyclopropylmethyl bromide and cyclopropylmethanethiol (Figure 2, Tables 2 and 3). Likewise, the $\nu(\text{C=C})$ mode at 1640 cm⁻¹ is clearly visible for 3-buten-1-yl formed from cyclopropylmethyl

(33) Carbon-bromine bond scission is expected to be facile on Mo(110) based on analogy with investigations of methyl iodide on Mo(110)³⁸ and ethyl iodide and bromide on Rh(111).³⁹ Furthermore, cyclopropylmethyl bromide reacts with oxygen to form the alkoxide based on the development of a C-O stretch mode at 1040 cm⁻¹ in the infrared spectrum. Such a reaction requires C-Br bond scission and lends credibility to our assertion of C-Br bond scission.

bromide annealed to 250 K on Mo(110),^{27,33} but is not detected for cyclopropylmethyl thiolate at 200 K, prior to hydrocarbon formation (Data not shown). Notably this fingerprinting in the C-H region required the resolution of infrared spectroscopy; such differences are not discernable with electron energy loss spectroscopy. The vibrational assignments were made by comparison to infrared assignments for gaseous and liquid cyclopropane and 1-butene adsorbed on Mo(110) (Figure 2, Tables 2 and 3).^{23,25}

Discussion

Reaction of thiolates via a cationic mechanism can be ruled out on the basis of the product distributions for both 3-butene-1-thiol and cyclopropylmethanethiol on Mo(110). The reactivities and the formation of the thiolate intermediates are qualitatively similar to other alkyl thiols investigated on Mo(110),¹ indicating that the mechanistic deduction applies broadly to thiols reacting on Mo(110). The cationic mechanism is ruled out because no rearrangement products are observed in the reactions of 3-butene-1-thiol and because no cyclobutane is observed in the reaction of either thiolate. *Ab initio* calculations show that the 3-buten-1-yl cation, which would be formed from heterolytic C-S bond scission of the 3-butene-1-thiolate, rearranges to cyclobutyl, cyclopropylmethyl and allyl cation (Scheme 2). The rearrangement occurs with zero activation energy in the gas phase, suggesting an extremely rapid rearrangement, perhaps even on the order of a vibrational period.¹⁴ The cyclopropylmethyl cation could in turn rapidly react with hydrogen to form methylcyclopropane. However, no methylcyclopropane was formed during 3-butene-1-thiolate reaction on Mo(110), providing strong evidence against a cationic mechanism. Similarly, no cyclobutane or cyclobutene is detected during the reactions of either 3-butene-1-thiolate or cyclopropylmethyl thiolate. Rearrangement to the cyclobutyl cation readily occurs in the gas phase for both the 3-buten-1-yl and cyclopropylmethyl cations. Hence, in addition to methylcyclopropane, cyclobutane and cyclobutene would also be produced if a cationic mechanism were involved.

The reactivity of both cyclopropylmethanethiol and 3-butene-1-thiol indicate that C-S bond scission and C-H bond formation occur nearly simultaneously based on the predominance of C-S bond hydrogenolysis without rearrangement (Figures 4 and 5). The lifetime of the cyclopropylmethyl radical, formed from homolytic C-S bond scission of cyclopropylmethyl thiolate, is on the order of 10⁻⁹ s in the gas phase.^{9,10} While the proximity of the surface might change the time scale, the predominance of methylcyclopropane formation from cyclopropylmethyl thiolate indicates that hydrogen addition must occur almost immediately upon C-S bond breaking. Rearrangement would lead to 1-butene and cyclobutane as hydrogenolysis products of cyclopropylmethyl thiolate, and neither are formed. The absence of rearrangement also indicates that, as for other thiols,¹ there is no C-S bond breaking below the temperature of hydrocarbon evolution. Carbon-sulfur bond scission followed by trapping on the surface is expected to lead to rearrangement on the surface, based on our investigations of cyclopropylmethyl bromide.

The observation of some rearrangement of the ring in the competing dehydrogenation process indicates that some cyclopropylmethyl radical is formed, however, and that a fraction of it is sufficiently long-lived that rearrangement to the 3-buten-1-yl radical occurs in the vicinity of the surface. β -Dehydrogenation of the resulting radical leads to 1,3-butadiene in a process similar to that observed for other thiolates on Mo(110) (Figure 4).

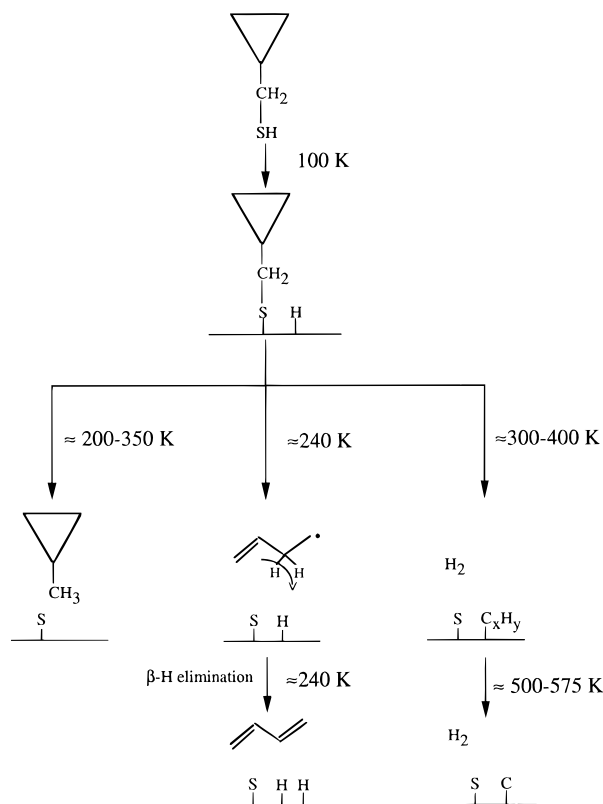


Figure 4. Proposed reaction scheme for cyclopropylmethanethiol on initially clean Mo(110).

Related studies of cyclopropylmethyl bromide also indicate that the rearrangement of the cyclopropylmethyl radical occurs in the vicinity of the surface.²⁷ Formation of a ring-opened alkyl via rearrangement of the hydrocarbon framework of cyclopropylmethyl bromide following C–Br bond scission on Mo(110)³³ is clearly indicated by the $\nu(\text{C}=\text{C})$ mode observed at 1640 cm^{-1} in the infrared spectrum obtained after heating to 250 K. Generally, alkyl halides are thought to react on surfaces via homolytic bond scission,^{34,35} and the observed rearrangement during cyclopropylmethyl bromide reaction is consistent with rapid rearrangement subsequent to the formation of the radical. Notably, no hydrocarbon products are evolved in subsequent temperature-programmed desorption of cyclopropylmethyl bromide, indicating that the trapped alkyl does not eliminate hydrocarbon products.²⁷

Interestingly, the relative yield of 1,3-butadiene, the product of C–S and C–H bond scission in both the 3-butene-1-thiolate and cyclopropylmethyl thiolate, is considerably lower than for any saturated thiol.^{3,4,27} However, the only other unsaturated thiol investigated on Mo(110), allyl thiol,³⁶ likewise reacts mainly via hydrogenolysis, suggesting that C–C bond unsaturation may play a role in determining the competition between nonselective reaction and β -dehydrogenation. Indeed, no volatile dehydrogenation product is produced from allyl thiol reaction on Mo(110).³⁶ These results suggest that trapping the nascent cyclopropylmethyl radical formed during C–S bond scission in the thiolates is favored relative to β -dehydrogenation. Indeed, it suggests that a significant amount of rearrangement may occur but that trapping and decomposition are favored over evolution of 1,3-butadiene.

The observation of some ring opening in the reactions of cyclopropylmethyl thiolate suggests that the hydrogenolysis may

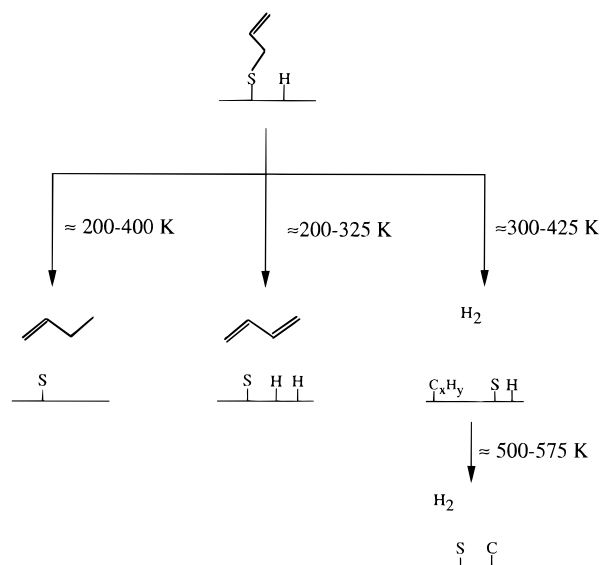


Figure 5. Proposed reaction scheme for 3-butene-1-thiol on initially clean Mo(110).

also proceed via an extremely short-lived radical. The addition of hydrogen to the cyclopropylmethyl radical would have to proceed on a time scale that is similar to the rearrangement, in order to be consistent with our results. Although the time scale for rearrangement in the vicinity of the surface is unknown and is not necessarily the same as in the gas phase, rearrangement of cyclopropylmethyl radical is expected to be rapid even in the presence of the Mo(110) surface. The reactivity of cyclopropylmethyl bromide supports this assertion, although it does not indicate the magnitude of the lifetime. The suppression of 1,3-butadiene formation by the presence of excess surface hydrogen is also consistent with this picture. However, hydrogen-assisted hydrogenolysis, whereby C–S bond breaking and C–H bond formation occur simultaneously, cannot be ruled out by our experiments, since the 1,3-butadiene may be formed via a path independent of the hydrogenolysis.

Interestingly, homolytic C–S bond cleavage during thiolate desulfurization has recently been shown to be induced by $\text{Cp}'_2\text{Mo}_2\text{Co}_2(\mu_3\text{-S})_2(\mu_4\text{-S})(\text{CO})_2$.³⁷ In the investigation of the mixed Mo–Co cluster, cyclopropylmethyl thiolate desulfurized with rearrangement to 1-butene. Kinetic measurements on the cluster indicated, however, that coordination of the thiolate to the cluster was rate-determining, not C–S bond scission which might partly explain the difference in the degree of rearrangement and product distributions for the cluster and the surface. On the other hand, the strong evidence for homolytic C–S bond scission both on Mo(110) and the mixed Mo–Co sulfide cluster suggests that this mechanism has a degree of generality for metal-induced desulfurization.

Conclusions

Rearrangement reactions were used to probe for short-lived intermediates in the reactions of cyclopropylmethanethiol and 3-butene-1-thiol on Mo(110). Thiolate intermediates were identified using vibrational spectroscopy, indicating facile S–H bond scission. Heterolytic C–S bond scission leading to a cationic intermediate is excluded, based on the lack of rearrangement products in the reactions of 3-butene-1-thiolate and the absence of cyclobutane or cyclobutene in the reactions of cyclopropylmethyl thiolate on Mo(110).

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Hydrogenolysis without rearrangement is the primary pathway for both thiols investigated. The lack of rearrangement in cyclopropylmethyl thiolate indicates that C–S bond scission and C–H bond formation occur nearly simultaneously. The production of a minor amount of 1,3-butadiene via rearrangement of a cyclopropylmethyl group in the reaction of cyclopropylmethyl thiolate indicates that homolytic C–S bond scission to afford the radical occurs to some extent. Related studies of cyclopropylmethyl bromide confirm that rearrangement is possible but that trapping of the cyclopropylmethyl radical is favored over selective β -dehydrogenation.

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