# Effect of Fluorination on Thiol Reactivity: Reaction of 2,2,2-Trifluoroethanethiol on Mo(110)

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The reactions of 2,2,2-trifluoroethanethiol on Mo(110) were studied using temperature-programmed reaction, Auger electron, and infrared spectroscopies. The chemistry of trifluoroethanethiol on Mo(110) is quite complex and significantly different than that observed for ethanethiol. Most significant is the evolution at 265 K of trifluoroethyl radical from a saturation coverage of  $CF_3CH_2S-$ . Ethyl radical was not detected in the reaction of ethanethiol on Mo(110). The strong coverage dependence for trifluoroethyl radical evolution and models depicting trifluoroethyl thiolate orientation at saturation coverage strongly suggest that surface crowding plays a significant role in radical formation. The stability of the radical and the steric inhibition to finding an adsorption site explain the evolution of the radical into the gas phase. C-S bond hydrogenolysis, yielding trifluoroethane, and defluorination, yielding difluoroethylene, are of nearly equal importance in the reaction of trifluoroethyl thiolate, whereas C-S bond hydrogenolysis of ethyl thiolate to form ethane predominates. The C-S bond hydrogenolysis pathway is similar for the two thiols, occurring at approximately 300 K in both cases. Dehydrogenation and alkene elimination from CH<sub>3</sub>CH<sub>2</sub>S- occur at approximately 340 K, as the supply of surface hydrogen is depleted through hydrogen recombination. In contrast, defluorination and fluoroalkene elimination from  $CF_3CH_2S$  – occur over a wide temperature range, 200–520 K. The relative facility of difluoroethylene formation is rationalized in thermodynamic terms. The formation of difluoroethylene on Mo(110) is nearly thermoneutral, due to the comparable strengths of the C-F and Mo-F bonds and the stability of difluoroethylene.

# Introduction

The reactions of methyl-terminated thiols have been previously studied on molybdenum and other single-crystal metals because of their relevance to catalytic desulfurization processes.<sup>1–10</sup> We undertook the investigation of fluorinated thiols—trifluoroethanethiol and trifluorobutanethiol—on molybdenum in order to probe the effect of fluorination on the thermal decomposition of alkanethiols and in order to fully understand the effect of electron exposure on methyl- and trifluoromethylterminated organic monolayers, described separately.<sup>11</sup> Molybdenum was chosen as the substrate because the chemistry of methyl-terminated thiols on Mo(110) is well-understood and also because of an increased interest in the use of refractory metals in electronic materials. This paper will focus on the chemistry of trifluoroethanethiol on Mo(110).

The S-H bond of the methyl-terminated thiols breaks facilely on Mo(110) to yield adsorbed alkyl thiolate (RS-) and atomic hydrogen.<sup>6-9</sup> The thiolate subsequently reacts through three pathways: 1. C-S bond hydrogenolysis to form alkanes; 2. dehydrogenation and desulfurization to form alkenes; 3. irreversible decomposition yielding gaseous dihydrogen and adsorbed carbon and sulfur. The irreversible decomposition pathway predominates at low coverages. Carbon-sulfur bond scission occurs between 300 and 400 K and limits the rate of hydrocarbon formation. The relative yields of alkane and alkene are partly determined by the amount of hydrogen present on the surface. Therefore, the relative yields of alkane and alkene depend on the temperature required for C-S bond breaking because hydrogen recombination commences at approximately 300 K.

We find that the addition of a trifluoromethyl head group significantly alters the reactivity of ethanethiol on Mo(110).

Trifluoroethyl thiolate is formed on Mo(110) at 100 K, resembling the low-temperature reaction of methyl-terminated thiols. The decomposition mechanism for the trifluoroethyl thiolate is strongly dependent on the coverage. Nonselective decomposition resulting in adsorbed sulfur, carbon, and fluorine and gaseous dihydrogen and hydrogen fluoride predominates at low coverage. At coverages below saturation, trifluoroethyl thiolate forms difluoroethylene in the range of 200-520 K, with peak maximums at 260 and 315 K, as well as trifluoroethane at 300 K. The defluorination reaction pathway is analogous to the dehydrogenation pathway of ethyl thiolate, leading to ethylene formation. The stronger C-F bond energy,  $\approx$ 115 kcal/ mol, relative to C-H bond energy, ≈90 kcal/mol, could lead one to conclude that fluorination might inhibit trifluoroethyl thiolate decomposition.<sup>12</sup> The driving force for the defluorination reaction is provided by the stronger Mo-F bond, relative to Mo-H bond and the increased thermodynamic stability of difluoroethylene when compared to ethylene. Hence, the defluorination reaction occurs readily. At saturation coverage, trifluoroethyl radical precedes trifluoroethane formation evolving at 265 K. The radical is only evolved over a very narrow coverage window,  $0.24 \le \theta \ge 0.26$  monolayer of thiolate.

# **Experimental Section**

Experiments were performed in an ultrahigh vacuum chamber, with a base pressure below  $1 \times 10^{-10}$  Torr. The chamber was equipped with a UTI quadrupole mass spectrometer, low-energy electron diffraction (LEED) optics, and an Auger electron spectrometer with cylindrical mirror analyzer (Perkin-Elmer, Model 15-155), all described previously elsewhere.<sup>13</sup>

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  $1 \times 10^{-9}$ 

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Torr of  $O_2$  for 5 min. The crystal temperature was allowed to return to  $\approx 200$  K and subsequently flashed to 2300 K for 30 s to remove the residual oxygen. No surface carbon or oxygen was detected in the Auger electron spectra of the surface recorded prior to fluorinated thiol adsorption. A sharp  $(1 \times 1)$ low-energy electron diffraction pattern was also observed.

The trifluoroethanethiol sample (Aldrich, 95%) was purified by vacuum distillation to remove any impurities. The samples were degassed by several freeze-pump-thaw cycles before each use. Dioxygen (Matheson, 99.8%), dihydrogen, and dideuterium were used as received.

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 sample was biased at -60 V in order to reflect electrons generated in the mass spectrometer and, therefore, preclude electron-induced decomposition.

All infrared reflection absorption spectra were collected using a single beam, clean-air-purged Fourier transform infrared spectrometer (Nicolet, Series 800) and averaged over 300 scans using an MCT detector at a 4 cm<sup>-1</sup> 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  $\approx 100$  K.

#### Results

**Temperature-Programmed Reaction Spectroscopy.** Three fluorocarbon products, 1,1-difluoroethylene, 1,1,1-trifluoroethane, and 1,1,1-trifluoroethyl radical, are produced during temperature-programmed reaction of a saturation coverage of trifluoroethanethiol (Figure 1). The only other gaseous products detected in a comprehensive search for products in the range of 2-250 amu were dihydrogen, H<sub>2</sub>, and hydrogen fluoride, HF. All products are observed at saturation coverage and identified by a quantitative analysis of mass spectrometer data, as described below.

1,1,1-Trifluoroethane is evolved at 300 K (Figure 1a, m/e = 69) and is identified by comparison to measurements made for an authentic sample of 1,1,1-trifluoroethane in our system. The trifluoroethane fragments m/e = 84, 69, 65, and 15 do not have contributions from the other products and were used to identify trifluoroethane, based on the close correspondence of their ratios for the product to an authentic sample of 1,1,1-trifluoroethane (Table 1). The mass spectrum of the 300 K product cannot be completely accounted for by trifluoroethane. Specifically, the relative intensities of m/e = 64, 45, 33, and 31 are too high and are attributed to a second product, 1,1-difluoroethylene. The rate of gaseous trifluoroethane formation is limited by the rate of reaction and not by the rate of trifluoroethane desorption. Trifluoroethane desorbs from Mo(110) below 200 K. (Data are not shown.)

1,1,1-Trifluoroethyl radical is evolved at 265 K. The radical was identified by the observation of m/e = 83 (CF<sub>3</sub>CH<sub>2</sub>), without observation of m/e = 84 (CF<sub>3</sub>CH<sub>3</sub>), the trifluoroethane parent, or any higher mass fragments in the 265 K state. At saturation coverage, the trifluoroethane parent, m/e = 84, is clearly observed at 300 K but not at 265 K (Figure 2). A reference mass fragmentation pattern was not available for comparison and can not be obtained from the fragmentation pattern of the product since trifluoroethyl radical and difluoroethylene evolution overlap at 265 K.<sup>14</sup> Difluoroethylene will be discussed in more detail below.

A detailed analysis of the line shape of the m/e = 64 spectrum at saturation coverage reveals that 1,1-difluoroethylene (Figure



**Figure 1.** Temperature-programmed reaction data following condensation of a trifluoroethanethiol multilayer on initially clean Mo(110). The spectra for the ions representative of the three fluorocarbon products are shown: (a) trifluoroethane, m/e = 69; (b) difluoroethylene and trifluoroethyl radical, m/e = 64 with the inset showing difluoroethylene evolution to 520 K; (c) trifluoroethyl radical, m/e = 83; (d) trifluoroethanethiol, m/e = 116; (e) dihydrogen, m/e = 2; (f) hydrogen fluoride, m/e = 20. The heating rate was nearly constant at 5 K/s in the range shown.

1b, m/e = 64) evolves over a wide temperature range, 200-520 K. Difluoroethylene evolves concurrently with both trifluoroethyl radical at 265 K and trifluoroethane at 300 K. All difluoroethylene fragments are also fragments of trifluoroethane and trifluoroethyl radical. The peak shapes indicate that two products are evolving in the 200-300 K temperature range (parts b and c of Figure 1). The leading edges of the peaks associated with difluoroethylene are significantly lower in temperature than that for the m/e = 83 peak, which is the parent mass for the trifluoroethyl radical. Analysis of the leading edge (230 K) of the difluoroethylene masses reveals a fragmentation pattern that closely corresponds to that measured for difluoroethylene. It does not match the pattern found for the overlap of trifluoroethyl radical and difluoroethylene at 265 K (Table 1). The shapes of peaks in the range of 300-350 K clearly indicate that there is a second product, in addition to triflu-

TABLE 1:	Fluorocarbon	Product I	Mass	Fragmentation	Patterns
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	mass fragments								
fluorocarbon	15	31	33	45	64	65	69	83	84
trifluoroethane <sup>a</sup>	30	13	12	16	8.5	27	100	0.4	0.25
difluoroethylene <sup>a</sup>		95	70	100	95				
difluoroethylene product <sup>b</sup>									
at 230 K		93	70	100	95				
at 300 K		94	75	100	92				
at 325 K		95	75	100	94				
trifluoroethane product <sup>c</sup>									
at 300 K	25					27	100		0.25
at 325 K	28					30	100		0.23
trifluoroethyl radical + difluoroethylene <sup>d</sup> at 265 K		95	65	92	100		10	5	

<sup>*a*</sup> An authentic sample as measured in our mass spectrometer. <sup>*b*</sup> The difluoroethylene mass fragmentation patterns at 300 and 325 K were corrected for trifluoroethane contribution. No correction was needed for the 230 K pattern. <sup>*c*</sup> The trifluoroethane mass fragmentation patterns at 300 and 325 K were corrected for difluoroethylene contribution. <sup>*d*</sup> Unable to correct the trifluoroethyl radical fragmentation pattern for difluoroethylene since the true difluoroethylene contribution at saturation coverage is unknown.



**Figure 2.** Temperature-programmed reaction data following condensation of trifluoroethanethiol on initially clean Mo(110). The spectra for (a) m/e = 84, CF<sub>3</sub>CH<sub>3</sub><sup>+</sup>, the trifluoroethane parent, and (b) m/e = 83, CF<sub>3</sub>CH<sub>2</sub><sup>+</sup>, the trifluoroethyl radical parent, are shown. The CF<sub>3</sub>CH<sub>3</sub> ion is clearly observed at 300 K but not at 265 K, while the CF<sub>3</sub>CH<sub>2</sub> ion evolves in two states at 265 and 300 K. Hence, the state at 265 K is representative of trifluoroethyl radical, whereas the 300 K peak is ascribed to trifluoroethane.

oroethane. Specifically, the masses unique to trifluoroethane, e.g., 69 amu, are narrower than those associated with difluoroethylene, e.g., 64 amu (parts a and b of Figure 1). Difluoroethylene was identified as the second product in the range of 300-350 K by subtracting the trifluoroethane contribution from the fragmentation pattern at two temperatures: 300 K, the trifluoroethane peak maximum, and 325 K, the trifluoroethane production at one-half of maximum (Table 1). The resulting fragmentation patterns at these two temperatures compare very favorably to that measured for an authentic difluoroethylene sample in our system. A trace amount of difluoroethylene

continues to evolve up to 520 K. The rate of gaseous difluoroethylene formation is limited by the rate of reaction and not by the rate of difluoroethylene desorption since it desorbs from Mo(110) below 220 K. (Data are not shown.)

Condensed layers of trifluoroethanethiol sublime from Mo(110) in a sharp peak at 120 K (Figure 1d, m/e = 116). This peak increases indefinitely with continued trifluoroethanethiol exposure, as expected. A small peak is also observed at 225 K and is ascribed to a minor amount of desorption from a second layer.

Dihydrogen is evolved at 320 and 540 K (Figure 1e, m/e = 2) and hydrogen fluoride at 315 and 535 K (Figure 1f, m/e = 20). The low-temperature hydrogen fluoride peak coincides with difluoroethylene evolution and is attributed to a recombination of adsorbed fluorine and thiol hydrogen. The low-temperature dihydrogen is attributed to the recombination of the thiol hydrogens. The high-temperature dihydrogen and hydrogen fluoride states must be due to nonselective decomposition of a surface intermediate containing both intact C-H and C-F bonds because of the extremely high temperature of dihydrogen evolution.

At saturation coverage, the amount of sulfur deposited was found to be  $0.26 \pm 0.01$  monolayer, based on the S(LMM) Auger electron intensity after heating condensed trifluoroethanethiol compared to the intensity measured for a 0.35monolayer sulfur overlayer.<sup>15</sup> The saturation coverage was confirmed to be  $0.26 \pm 0.01$  monolayer of thiolate, based on the sulfur desorption yield at high temperature, 1400-2080 K. The integrated area under the sulfur peaks following trifluoroethanethiol reaction was compared to that for a 0.35 monolayer sulfur coverage, to derive a saturation coverage of  $0.26 \pm 0.01$ monolayer. Residual carbon and fluorine were also detected by Auger electron spectroscopy following temperature-programmed reaction to 750 K.

The distribution of products evolved during temperatureprogrammed reaction of trifluoroethanethiol on initially clean Mo(110) depends strongly on the trifluoroethanethiol exposure (Figure 3).<sup>16</sup> At the lowest coverages studied,  $\theta \le 0.1$ monolayer of thiolate, 1,1-difluoroethylene is the only fluorocarbon product formed, evolving at 270 K. Dihydrogen evolves over a broad range centered at 410 K, with a less intense hightemperature shoulder at 515 K. (Data are not shown.) Hydrogen fluoride, trifluoroethane, and trifluoroethyl radical are not detected at this low coverage. At intermediate coverages between,  $0.1 \le \theta \le 0.23$  monolayer of thiolate, 1,1,1trifluoroethane, and 1,1-difluoroethylene are evolved near 300 K. 1,1-Difluoroethylene is also still observed at 260 K. Hydrogen fluoride and dihydrogen are also detected within this coverage range, dihydrogen at 320 and 540 K and hydrogen



Figure 3. Relative product yields as a function of sulfur coverage for (a) trifluoroethane, (b) difluoroethylene, (c) trifluoroethyl radical, and (d) hydrogen fluoride. The relative yields were calculated by dividing the peak height at each sulfur coverage by the maximum peak height observed for each species. The error bars indicate one standard deviation based peak height measurements of five or more temperature-programmed reaction spectra.

fluoride at 315 and 535 K. The yields of hydrogen fluoride (Figure 3d) and difluoroethylene (Figure 3b) are maximized at a thiolate coverage of  $\approx 0.23$  monolayers; no trifluoroethyl radical is evolved up to this coverage. The trifluoroethane yield is maximized at  $\theta = 0.26$  monolayers (Figure 3a). Trifluoroethyl radical evolution is first observed at a coverage of 0.24 monolayers, with the yield increasing up to saturation, 0.26 monolayers (Figure 3c). The production of HF decreases by approximately 35% in the range of 0.24–0.26 monolayers (Figure 3d). At saturation coverage, difluoroethylene is mainly produced at  $\approx 315$  K. The difluoroethylene contribution to the radical peak at 265 K is difficult to quantify due to the overlap in the fragmentation patterns of the two products and the lack of reference data for trifluoroethyl radical.

Nonselective decomposition affording atomic carbon, fluorine, sulfur, gaseous dihydrogen, and gaseous hydrogen fluoride is a competing pathway. Carbon, fluorine, and sulfur remain on the surface at all coverages, as determined by Auger electron spectroscopy. The carbon signal intensity is at a maximum at  $\theta \approx 0.15$  monolayer of thiolate. The fluorine signal intensity is at a maximum at  $\theta \approx 0.23$  monolayer of thiolate, when the difluoroethylene yield is at a maximum. Both the fluorine and carbon signals decrease at saturation coverage by approximately 35% from their maximum values.

The presence of adsorbed deuterium and hydrogen significantly alters the product distribution for trifluoroethanethiol and decreases the saturation coverage. When a saturation coverage of deuterium or hydrogen is adsorbed on Mo(110), prior to trifluoroethanethiol exposure, the maximum amount of thiolate formed is only 0.18 monolayers, compared to 0.26 monolayers on the clean surface. In addition, trifluoroethane is the major fluorocarbon product evolving at 300 K. The yield of trifluoroethane evolving from the deuterium- or hydrogen-precovered surface increased by approximately 35% when compared to the yield from the clean surface for similar thiolate coverages. No trifluoroethyl radical, CF<sub>3</sub>CH<sub>2</sub>, or difluoroethylene, CF<sub>2</sub>CH<sub>2</sub>, is detected at 265 K when H or D is adsorbed prior to the thiol. The difluoroethylene peak at 315 K is also significantly reduced in intensity relative to trifluoroethane formation, when H or D is present, based on changes in the ratios of the mass fragments characteristic of difluoroethylene (64 amu) and trifluoroethane (69 amu). The (m/e = 64):(m/e = 69) ratio is 0.34 for reaction on the initially clean surface compared to 0.11 for the hydrogenor deuterium-saturated surface. Hydrogen fluoride at 315 K is also reduced in intensity relative to the initially clean surface and HF is no longer observed at 520 K, when hydrogen is preadsorbed. No DF is detected, only one deuterium is incorporated in the trifluoroethane product, and no deuterium



Figure 4. Reflection infrared spectra of CF<sub>3</sub>CH<sub>2</sub>S- at (a) submonolayer,  $\theta = 0.1$  ML, and (b) saturation coverages,  $\theta = 0.25$  ML.

TABLE 2: Vibrational Assignments for CF<sub>3</sub>CH<sub>2</sub>SH

assignment	multilayer, 100 K CF3CH2SH	monolayer, $\theta = 0.25$ ML, 100 K CF <sub>3</sub> CH <sub>2</sub> S -	CF <sub>3</sub> CH <sub>2</sub> Cl (liquid) <sup>17</sup>
$\overline{\nu_{a}(CH_{2})}$	3015		3044
$\nu_{\rm s}$ (CH <sub>2</sub> )	2965		2992
$\nu$ (S-H)	2550		
$\delta$ (CH <sub>2</sub> ) scissors	1478	1467	NR
TW (CH <sub>2</sub> ) twist	1419	1410	1440
$\nu_{\rm a}({\rm CF}_3)$	1325		
$\nu_{\rm a}$ (CF <sub>3</sub> )	1302	1305	1277
$\nu$ (C-C) + $\gamma$ (CF <sub>3</sub> )			1210
$\nu_{\rm s}$ (CF <sub>3</sub> )	1150	1150	1159
$\nu$ (C-C)	845		855

is incorporated into difluoroethylene, indicating that no lowtemperature H-D exchange is occurring, when deuterium is adsorbed prior to trifluoroethanethiol. The absence of hightemperature DF and the reduction in the integrated yield of all dihydrogen isotopes at high temperature indicates that preadsorption of deuterium significantly abates both irreversible decomposition and difluoroethylene formation. Site blocking by H(D), denying fluorines access to the molybdenum surface, could, in part, explain the absence of difluoroethylene at 260 K and the reduction in difluoroethylene at 315 K.

Infrared Spectroscopy. Low-temperature S-H bond scission leading to the formation of trifluoroethane thiolate, CF<sub>3</sub>- $CH_2S-$ , on the Mo(110) surface is proposed, in analogy to methyl-terminated thiols. Only four distinct features, all below 1500 cm<sup>-1</sup>, are observed for a saturation exposure in the reflection infrared spectrum collected at 100 K (Figure 4b and Table 2). The two intense features at 1305 and 1150  $cm^{-1}$  are assigned to the asymmetric and symmetric C-F stretches, respectively. The two weak features at 1470 and 1410 cm<sup>-1</sup> are assigned to the CH<sub>2</sub> scissor and twist deformations, respectively. These assignments compare favorably with assignments made for gas phase CF<sub>3</sub>CH<sub>2</sub>Cl,<sup>17</sup> as well as data for multilayers of CF<sub>3</sub>CH<sub>2</sub>SH (Table 2). No value was reported for the CH<sub>2</sub> scissors mode in CF<sub>3</sub>CH<sub>2</sub>Cl, but this mode is generally observed at  $\approx 1470$  cm<sup>-1</sup> in hydrocarbons and in condensed films of hydrocarbon polymers with fluorocarbon side chains.<sup>18,19</sup> The asymmetric and symmetric C-F stretches of the thiolate at 1305 and 1150 cm<sup>-1</sup> are similar in energy to those for the condensed thiol. An additional asymmetric C-F stretch mode is also observed at 1325 cm<sup>-1</sup> for the condensed thiol.<sup>20</sup> The mode at 2550  $cm^{-1}$  is assigned to the S-H stretch and is not observed for coverages below saturation, consistent with S-H bond cleavage and thiolate formation.<sup>21</sup> The modes at 3015 and 2965  $cm^{-1}$  are assigned to the asymmetric and symmetric C-H stretch of methylene, respectively, based on comparison to the CF<sub>3</sub>CH<sub>2</sub>Cl assignments.<sup>17</sup> The methylene C-H stretch modes are also not observed for coverages below

saturation. The rather high  $v(CH_2)$  modes compared to  $CH_3$ -terminated thiols<sup>17,22-25</sup> are due to the presence of fluorine at the adjacent carbon. The mode at 845 cm<sup>-1</sup> is assigned to a C-C stretch and compares favorably with the C-C stretch assignment of 855 cm<sup>-1</sup> made for CF<sub>3</sub>CH<sub>2</sub>Cl.<sup>17</sup>

The relative intensities of the symmetric and asymmetric C-F stretches vary with trifluoroethanethiol exposure (parts a and b of Figure 4). The frequencies of both the symmetric and asymmetric CF<sub>3</sub> stretch modes also shift to somewhat lower energy as the thiolate coverage decreases (Figure 4 and Table 2). At the lowest coverages investigated ( $\theta < 0.1$  monolayer of thiolate), the C-F symmetric stretch,  $1140 \text{ cm}^{-1}$ , is more intense than the C-F asymmetric stretch, 1290  $cm^{-1}$  (Figure 4a). As the coverage is increased ( $\theta \approx 0.25$  monolayer of thiolate), there is a significant change in the intensity of the C-F modes with the asymmetric stretch becoming more intense (Figure 4b). The change in relative intensity shifts gradually throughout this coverage range and suggests either a coveragedependent change in the orientation of the molecule or a change in the dynamic dipole moment of the CF<sub>3</sub> modes upon thiolate formation. Since the frequency of the C-F modes is not perturbed significantly upon formation of the thiolate, CF<sub>3</sub>- $CH_2S-$ , and since the bonding to the surface is via the sulfur atom, it is reasonable to assume that the relative dipole moments of these modes are also not dramatically changed from the condensed phase, even if their absolute values are altered. This assumption has been validated for  $CH_3O$  on Mo(110), for which the CH<sub>3</sub> orientation was estimated with both IR and NEXAFS.<sup>26</sup> The orientation of the trifluoromethyl group can be estimated by comparing the relative intensities of the C-F symmetric and asymmetric modes of the multilayer, assumed to have no preferred orientation, to their ratios at a specific thiolate coverage. Upon going from submonolayer to monolayer coverages, the relative intensities of the C-F modes  $(v_s/v_a)$ change from 0.65 to 1.25, respectively, compared to 1.12 for the multilayer. This corresponds to a change in the trifluoromethyl group orientation of approximately 20°, a shift from a 40° tilt with respect to the surface normal at low coverages ( $\theta$  $\approx 0.1$ ) to approximately 60° away from surface normal at saturation coverage (Figure 5).<sup>27</sup> While the estimated orientations are subject to our assumptions, the data clearly demonstrate that there is a reorientation of the  $CF_3$  group as the coverage is increased. Notably, the reorientation is complete at the coverage required for CF<sub>3</sub>CH<sub>2</sub>• evolution. The orientation observed for  $\theta = 0.1$  monolayers of thiolate cannot persist for coverages on the order of  $\theta \approx 0.2$  monolayer and above because the CH<sub>2</sub> groups, which reside in the plane of the sulfurs, overlap with the sulfur atoms of the neighboring thiolates (Figure 5c). The methylene symmetric and asymmetric stretch modes were not observed at coverages below saturation due to their relatively





b) saturation coverage,  $\theta$ =0.25 ML



c) representation of submonolayer orientation at saturation coverage



d) Overlap between thiolate and radical at 280 K



**Figure 5.** Scale model of CF<sub>3</sub>CH<sub>2</sub>S- on Mo(110) illustrating steric effects in reorientation: (a) side view of submonolayer coverage ( $\theta = 0.1$  ML); (b) side view of saturation coverage ( $\theta = 0.25$  ML); (c) side view of the submonolayer orientation at saturation coverage representing the overlap of sulfurs and alkyl chains that would occur if the low-coverage geometry were preserved at saturation; (d) representation of overlap between the intact thiolate and the radical formed following low-temperature C-S bond scission. The orientations depicted are based on the coverage-dependent changes observed in the C-F symmetric and asymmetric stretches. The molecular structure of the thiolate is the same in all cases with the S-C-C bond remaining constant and the Mo-S-C bond changing with orientation.

low intensity and could not be used to independently probe the thiolate orientation.

An additional vibrational mode at 1220 cm<sup>-1</sup> is observed at low trifluoroethane thiolate coverage ( $\theta = 0.1$  monolayer, Figure 4a) that is not observed for condensed CF<sub>3</sub>CH<sub>2</sub>SH or CF<sub>3</sub>CH<sub>2</sub>-Cl. At 100 K, the 1220 cm<sup>-1</sup> mode correlates with the symmetric stretch, becoming less intense as the molecule reorientates and the C-F symmetric stretch decreases in intensity relative to the asymmetric stretch. An unequivocal assignment for the mode at 1220 cm<sup>-1</sup> is difficult due to the complexity of the trifluoroethane thiolate reflection infrared spectra. Two possible assignments can be considered for the 1220 cm<sup>-1</sup> mode. One assignment is a combination band of the C-C stretch at 854 cm<sup>-1</sup> and a CF<sub>3</sub> rock at approximately 360 cm<sup>-1</sup> in Fermi resonance with the C-F fundamental.<sup>17</sup> Due to the low frequency of the CF<sub>3</sub> rock, it cannot be observed with our infrared configuration. Alternatively, this mode may be due to a C-F stretch of a CF2 group.<sup>28-31</sup> The CF2 asymmetric stretch is observed at 1215 and 1222 cm<sup>-1</sup> for poly-(tetrafluoroethylene) and isolated CF<sub>2</sub> free radical, respectively.<sup>31,32</sup> The observation of a CF<sub>2</sub> could be the result of a low-temperature defluorination reaction.

# Discussion

Trifluoroethanethiol is proposed to form trifluoroethanethiolate (CF<sub>3</sub>CH<sub>2</sub>S-) on Mo(110) after low-temperature S-H bond scission, analogous to the low-temperature reaction of ethanethiol on Mo(110). However, the chemistry of trifluoroethanethiol is quite complex and substantially different from ethanethiol. The reactivity and structure of the thiolate strongly depend on coverage; specifically, steric effects are proposed to lead to trifluoroethyl radical evolution. The trifluoroethanethiol reacts at saturation coverage via four competing pathways: (1) C-S bond hydrogenolysis at 300 K to yield trifluoroethane; (2)  $\gamma$ -fluorine elimination in the range of 200-520 K to yield difluoroethylene; (3) C-S bond scission at 265 K to yield trifluoroethyl radical; (4) irreversible decomposition, ultimately resulting in H<sub>2</sub> and HF and adsorbed carbon, sulfur, and fluorine (Figure 6).

Trifluoroethyl radical is produced at 265 K, at CF<sub>3</sub>CH<sub>2</sub>Scoverages near saturation, in addition to trifluoroethane, difluoroethylene, dihydrogen, and hydrogen fluoride. The radical was formed over a very narrow coverage range, 0.24-0.26 monolayers of thiolate, the same coverage range where the CF<sub>3</sub> reorientation is complete. The trifluoroethyl radical state saturates as the multilayer begins to form and consequently must be surface mediated. The narrow coverage window and the correlation with the IR data suggest that surface crowding allows the trifluoroethyl radical formed to desorb. X-ray photoelectron data for CH<sub>3</sub>CH<sub>2</sub>S- indicated that C-S bond scission is initiated at approximately 270 K at saturation coverage but is not totally complete until approximately 400 K.7 This is nearly the same temperature at which trifluoroethyl radical evolution is observed in the reaction of CF<sub>3</sub>CH<sub>2</sub>S- suggesting that the C-S bonds are broken with similar facility for both methyl- and trifluoromethyl-terminated thiolates.

As depicted in our model for a saturated layer of CF<sub>3</sub>CH<sub>2</sub>S-(Figure 5b), the interaction of the trifluoroethyl radical, formed from C-S bond scission, with the surface is sterically inhibited, due to the extreme crowding. Formation of a Mo-CH<sub>2</sub>CF<sub>3</sub> bond will be effectively blocked because of the overlap between the CF<sub>3</sub> group of the radical and the intact thiolate (Figure 5d). The stability of the radical, with a heat of formation for CF<sub>3</sub>-CH2 of -123.6 kcal/mol and the steric constraints to radical adsorption, explains gas-phase radical evolution from the sterically crowded surface.<sup>12</sup> Radical evolution is not observed for ethyl thiolate, CH<sub>3</sub>CH<sub>2</sub>S-, even though the saturation coverage for the two molecules is equivalent.33 Two factors are contributing to the absence of ethyl radical formation. Firstly, ethyl radical is significantly less stable than trifluoroethyl radical, with a heat of formation for CH<sub>3</sub>CH<sub>2</sub>• of 25.6 kcal/mol compared to -123.6 kcal/mol for CF<sub>3</sub>CH<sub>2</sub><sup>.12</sup> In addition, the amount of CH3CH2S-, which irreversibly decomposes, is approximately 30% higher than the amount of CF3CH2Sirreversible decomposition at similar coverages.<sup>34</sup> An increase in the amount of irreversible decomposition leads to less intact ethyl thiolate on the surface at saturation and therefore less steric inhibition. The difference in the irreversible decomposition pathway for the two molecules is most likely due to an increase in the methylene C-H bond strength for trifluoroethyl thiolate. Alternatively, the steric factors may be different in the two cases. The structures of CF3CH2S- and CH3CH2S- could be significantly different, in particular at high coverage, given that the CF<sub>3</sub> group has a significantly higher dipole moment. The tilt



Figure 6. Proposed reaction scheme for trifluoroethanethiol on initially clean Mo(110).

angle at high coverages may represent a structure that minimizes dipole-dipole repulsions. Indeed,  $CF_3(CF_2)_7(CH_2)_2SH$  packs more densely than  $CH_3(CH_2)_9SH$  on Au based on tilt angles of 16° and 27°, respectively, with respect to the surface plane.<sup>24</sup> These results suggest that a similar effect may lead to different steric effects in  $CH_3CH_2S$ - compared to  $CF_3CH_2S$ - on Mo(110). Unfortunately, data are not available on the structure of  $CH_3CH_2S$ - on Mo(110). The relatively larger dipole moment in the F-terminated group could also enhance desorption of the radical in that the nascent radical may be repelled by neighboring  $CF_3CH_2S$ - groups.

The decrease in HF production, in the coverage range of trifluoroethyl radical formation, provides additional evidence for an overall structural transformation leading to a different reactivity.  $CF_3CH_2S-$ , which would have decomposed through fluorine elimination or the irreversible decomposition pathways, are ejected as radicals, decreasing the amount of fluorine eliminated to the surface and HF production at saturation coverage. Auger electron spectroscopy also shows an approximate 35% decrease in carbon adsorbed on the surface. In contrast, the amount of carbon deposited from ethanethiol decomposition monotonically increases with thiolate coverage;  $CH_3CH_2^{\bullet}$  is *not* produced from  $CH_3CH_2S-$  at any coverage. These data demonstrate the correlation between radical evolution and the decrease in nonselective decomposition at high  $CF_3$ - $CH_2S-$  coverages.

Fluorocarbon and hydrocarbon radical formation have also been reported for several other heterogeneous reactions. Trifluoromethyl iodide decomposes on Pt(111) and Ru(001) forming  ${}^{\circ}CF_3$  and  $:CF_2.^{35,36}$  The temperature at which these radicals form and the yield are dependent on both the metal and coverage. The formation of gaseous methyl radicals has also been reported during the decomposition of CH<sub>3</sub>I on clean Cu(111)<sup>37</sup> and CH<sub>3</sub>O- on oxygen-precovered Mo(110).<sup>38</sup> The heat of formation for methyl radical, CH<sub>3</sub>•, is +34.0 kcal/mol.<sup>12</sup> The observation of methyl radicals, which have positive heats of formation, suggests that fluorocarbon radical formation is probable.

At low coverages, difluoroethylene formation and nonselective decomposition predominate, whereas trifluoroethane and trifluoroethyl radical formation become important as the coverage increases (Figure 3). C-S bond hydrogenolysis of ethyl thiolate to form ethane predominates, whereas C-S bond hydrogenolysis to form trifluoroethane and defluorination to form difluoroethylene are of nearly equal importance in the reaction of trifluoroethyl thiolate. The C-S bond hydrogenolysis pathway is similar for the two thiols, occurring at approximately 300 K in both cases. Therefore, the different product distributions must be due to differences in the reactivity of the alkyl group, not to differences in the facility for C-Sbond scission. Dehydrogenation and alkene elimination from  $C_2H_5S$  – occur at  $\approx 340$  K as the surface hydrogen was depleted through hydrogen recombination and as the rate of C-S bond hydrogenolysis decreased. In contrast, defluorination and alkene elimination from CF<sub>3</sub>CH<sub>2</sub>S- to form difluoroethylene occur over a wide temperature range, 200-520 K, spanning a range

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below to above the trifluoroethane formation, peaking at 260 and 315 K. Gaseous dihydrogen and hydrogen fluoride evolution and the deposition of carbon, fluorine, and sulfur were the result of nonselective decomposition.

Difluoroethylene production effectively competes with trifluoroethane formation. The 315 K CF<sub>2</sub>CH<sub>2</sub> peak resembles the pattern of  $CH_2CH_2$  production from ethanethiol on Mo(110); both  $CH_2CH_2$  and  $CF_2CH_2$  are formed at slightly higher temperatures than the corresponding alkanes and can be ascribed to a decrease in hydrogenolysis due to a depletion of surface hydrogen. The low-temperature state, due to defluorination, may be possible because of the availability of sites for radical adsorption and the tilted geometry, which may facilitate C-Sbond breaking (Figure 5a). There is no alkene production from CH<sub>3</sub>CH<sub>2</sub>S-, analogous to low-temperature (270 K) difluoroethylene. At  $\theta \approx 0.1$  monolayer, where CF<sub>3</sub>CH<sub>2</sub>S- either irreversibly decomposes or reacts to form difluoroethylene, only irreversible decomposition of  $CH_3CH_2S$  – occurs. In fact, the carbon coverage following temperature-programmed reaction to 750 K is approximately 30% higher for CH<sub>3</sub>CH<sub>2</sub>S- compared to CF<sub>3</sub>CH<sub>2</sub>S-, at initial coverages of 0.1 monolayer. We propose that fluorine inhibits nonselective decomposition at low coverages due to an increase in the strength of the methylene C-H bonds and greater stability of difluoroethylene.<sup>12</sup> The predominance and relative facility of difluoroethylene formation, compared to the methyl-terminated case, can be rationalized in thermodynamic terms. The formation of difluoroethylene is nearly thermoneutral on the molybdenum surface due to the comparable strengths of the C-F and Mo-F bonds and the stability of the difluoroethylene product.<sup>12,39</sup> The heat of formation for difluoroethylene is -77.5 kcal/mol, in contrast with a heat of formation of +12.5 kcal/mol for ethylene.<sup>12</sup> Fluorination also stabilizes the fluoroalkyl intermediates leading to high-temperature products. For example, difluoroethylene evolves up to 520 K, but high-temperature evolution of ethylene was not observed for CH<sub>3</sub>CH<sub>2</sub>S- decomposition.

Preadsorbed deuterium significantly alters the product distribution of trifluoroethanethiol. On the preadsorbed deuterium surface, trifluoroethane is the major product. Neither the lowtemperature difluoroethylene nor the trifluoroethyl radical states was observed. The 315 K difluoroethylene state is still observed but significantly reduced in intensity relative to trifluoroethane. Because of the effectiveness with which fluorine elimination competes with C-S bond hydrogenolysis, the effect of predeuteration of the Mo surface is quite pronounced for trifluoroethanethiol. In the case of predeuteration, the deuterium acts as a site blocker, blocking both the ability to form the thiolate and the accessibility of the trifluoromethyl group to the surface. With presaturation of the surface, no deuterium was incorporated into the difluoroethylene and one deuterium was incorporated into the trifluoroethane.

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