

# Effect of Coadsorbed Species and Temperature on Competitive Reaction Channels for Nascent Radicals: *c*-C<sub>3</sub>H<sub>7</sub>CH<sub>2</sub>SH on Mo(110)–(6 × 1)-O

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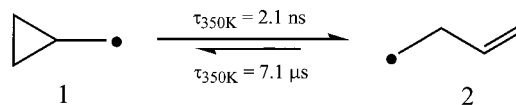
The reaction of cyclopropylmethanethiol on oxygen-modified Mo(110) is studied as a means of probing for radical species and their residence times on surfaces. A thiolate species and a surface hydroxyl group, OH<sub>a</sub>, form upon adsorption of cyclopropylmethanethiol on O-covered Mo(110). Near 200 K, homolytic cleavage of the thiolate C–S bond occurs, yielding the methylcyclopropyl radical. The radical abstracts hydrogen from OH<sub>a</sub> and desorbs without rearrangement as methylcyclopropane. Between 300 and 350 K, trapping of the ring-closed radical by surface oxygen via C–O bond formation competes efficiently because of an increasing number of free oxygen sites, resulting in a surface covered with methylcyclopropoxide species. Reactions of the cyclic alkoxide are similar to those observed for the O analogue hydroxymethylcyclopropane; it undergoes C–O bond scission, rearranges to the butenyl radical, and forms linear alkoxide and alkyl species between 350 and 430 K. However, the sulfur deposited by C–S bond cleavage (~0.2 monolayer) leads to complete suppression of nonselective decomposition. Assuming that the rate constant for rearrangement on the surface is similar to that in solution, limits are estimated for the rate constants for hydrogenation and trapping:  $k_{\text{hydrogenation}}(200 \text{ K}) > 2.5 \times 10^6 \text{ s}^{-1}$ ,  $k_{\text{hydrogenation}}(350 \text{ K}) < 4.73 \times 10^8 \text{ s}^{-1}$ ,  $k_{\text{trap}}(350 \text{ K}) > 4.73 \times 10^8 \text{ s}^{-1}$ , and  $k_{\text{trap}}(430 \text{ K}) < 30.7 \times 10^8 \text{ s}^{-1}$ . Comparison with reaction of cyclopropylmethanethiol on clean Mo(110) reveals that modification of the surface with oxygen reduces the amount of desulfurization by 35% to 40%. Further, it opens a new reaction channel, i.e., C–O bond formation, and completely suppresses the 25% of complete decomposition observed on clean Mo(110).

## Introduction

Hydrocarbon radicals have been of interest to the chemical community for as long as 100 years since the first report<sup>1</sup> of a long-lived triphenyl radical by Gomberg in 1900.<sup>2</sup> Because of their reactive nature, radicals are usually formed only as short-lived intermediates during chemical transformations. Their transient nature renders their detection rather challenging. In 1980 Griller and Ingold<sup>3</sup> introduced the new concept of *free radical clocks* to organic solution-phase chemistry, which resulted in a new field, i.e., radical–molecule reaction kinetics.<sup>4,5</sup> A free radical clock can be understood as an intramolecular rearrangement on a known time scale that involves a radical center. Reaction of the rearranging radical with a radical of unknown lifetime and careful analysis of the product distribution yield the lifetime of the unknown radical. Today, a large number of free radical clocks are available with rate constants ranging from 10<sup>2</sup> to 10<sup>11</sup> s<sup>−1</sup>.<sup>5,6</sup>

Radicals are also often postulated as reactive intermediates in many surface reactions. They are thought to be important in reactions of halocarbons with metal surfaces,<sup>7</sup> in desulfurization of linear, branched, and cyclic thiols,<sup>8,9</sup> in C–C coupling reactions,<sup>10–12</sup> and in reduction of alcohols<sup>13</sup> on metal surfaces. Homolytic C–S bond cleavage leading to formation of a hydrocarbon radical has been proposed as the rate-determining step in desulfurization of thiols on the basis of the observation that the temperature required for olefin production correlates with homolytic C–S bond dissociation energies of various

## SCHEME 1



thiols. Furthermore, coadsorption studies of linear thiols and cyclic sulfides such as triethylene sulfide<sup>8,9,14</sup> clearly demonstrated that ring opening, i.e., C–S bond scission, plays an important role in determining the kinetics and selectivity for Mo-catalyzed dehydrosulfurization processes.

Despite the large interest in radical species on surfaces, techniques for their detection are limited. Electron spin resonance, a technique commonly used for detection of unpaired spins in solution phase, cannot be applied to bare metal surfaces because of screening by the metal. Thus, we have started to explore the possible application of free radical clocks as a means for radical detection and residence time measurements on surfaces. The reactions of hydroxy-<sup>15</sup> and bromomethylcyclopropane<sup>16</sup> on oxygen-modified Mo(110) have recently been reported. Hydroxymethylcyclopropane forms a cyclic alkoxide species via O–H bond cleavage upon adsorption onto oxygen-covered Mo(110). The cyclic alkoxide is stable up to 400 K, where the C–O bond breaks and the methylcyclopropyl radical **1** forms and rearranges to the linear, ring-opened butenyl radical **2** in the vicinity of the surface (Scheme 1). The butenyl radical is trapped by either surface oxygen or exposed Mo atoms to form the linear alkoxide or alkyl intermediates, respectively,

on the surface. Heating to 500 K causes the C–O and C–Mo bonds to break, yielding 1-butene, 1,3-butadiene, and ethene via hydrogen abstraction and  $\beta$ -hydrogen elimination in a 22:60:18 ratio.

A similar mechanism has been proposed for the reaction of bromomethylcyclopropane;<sup>16</sup> however, there is a distinct difference in the mechanism of the Br analogue at lower temperatures evolving around the steps of C–Br bond cleavage and C–O bond formation. A substitution mechanism has been proposed as an alternative to homolytic cleavage of the C–Br bond, which would involve the formation of a transient radical species. The latter seems to be less likely because no ring opening of the radical species is observed at temperatures below 300 K. However, the reaction rate constant for ring opening decreases by an order of magnitude from 400 to 300 K;<sup>17</sup> thus, the absence of ring opening in the bromomethylcyclopropane case could be due to the slow rate of rearrangement at 300 K. The sulfur analogue of hydroxymethylcyclopropane (i.e., cyclopropylmethanethiol) is a suitable test system for the above-mentioned mechanistic question because homolytic cleavage of the C–S bond, i.e., radical formation, occurs near  $\sim$ 300 K on clean Mo(110),<sup>18,19</sup> a temperature higher than that for C–Br bond dissociation. Furthermore, the C–O bond is stronger than the C–S bond; therefore, oxygen substitution would be thermodynamically favorable.

In the following we present results from the reaction of cyclopropylmethanethiol on oxygen-covered Mo(110). Temperature-programmed reaction, X-ray photoelectron spectroscopy, and reflection–absorption infrared data provide evidence that cyclopropylmethanethiol forms a thiolate upon adsorption onto O-modified Mo(110) at 100 K. C–S bond cleavage commences at 200 K, the onset of methylcyclopropane formation, and is completed by 350 K. The presence of oxygen on the surface opens a new, competitive pathway, i.e., C–O bond formation, leading to a surface-bound, ring-closed alkoxide at 350 K. The latter undergoes the methylcyclopropyl–butenyl radical rearrangement to the linear alkoxide species above 350 K as reported recently for the hydroxymethylcyclopropane precursor.<sup>15</sup>

## Experimental Details

Infrared and temperature-programmed reaction experiments are performed in an ultrahigh vacuum chamber with a base pressure of  $\leq 1 \times 10^{-10}$  Torr, described previously.<sup>13,20</sup> The chamber is equipped with a UTI quadrupole mass spectrometer, low-energy electron diffraction (LEED) optics, and an Auger spectrometer with a cylindrical mirror analyzer (Perkin-Elmer model 15-555). The infrared spectra are collected using a single beam, clean air purged Fourier transform infrared spectrometer (Nicolet, series 800) and averaged over 500 scans using an MCT detector at  $4 \text{ cm}^{-1}$  resolution, the scan time being approximately 3.5 min. Sample spectra are ratioed against a background that is taken immediately after the sample scan by flashing the crystal to 760 K. The background scan is initiated after the crystal temperature has returned to  $\sim$ 130 K. This procedure reveals only irreversible chemical transformations.

The crystal is positioned approximately 2 mm from the aperture (3 mm) of the mass spectrometer shield during the collection of temperature-programmed reaction data. The crystal is biased at  $-100 \text{ V}$  during temperature-programmed reaction to minimize reactions induced by electrons from the mass spectrometer filament. The mass spectrometer is interfaced with a computer, and data are collected with a program, which allows collection of up to 16 separate ion intensity profiles during a

single experiment. The heating rate is nearly constant with  $\Delta T/\Delta t = (10 \pm 2) \text{ K/s}$  between 110 and 760 K.

The Mo(110) crystal can be cooled to 100 K, heated to 760 K radiatively, or heated to 2300 K by electron bombardment. The Mo(110) surface is cleaned before each experiment by oxidation at 1200 K in  $1 \times 10^{-9}$  Torr of  $\text{O}_2$  for 2 min. The crystal temperature is allowed to return to  $\sim$ 200 K and subsequently (three times) flashed to 2300 K to remove residual oxygen. No surface carbon or oxygen is detected in the Auger electron spectra of the surface recorded after cleaning.

Preparation and characterization of the oxygen overlayer ( $\Theta_{\text{O}} = 0.67$  monolayer (ML)) used in this study have been outlined in detail previously.<sup>21,22</sup> Briefly, the Mo(110) crystal is saturated with  $\text{O}_2$  at 100 K. Subsequent heating of the surface to 500 K results in an overlayer with oxygen predominantly in low-symmetry, high-coordination sites.<sup>23</sup> The coverage of this overlayer is  $\Theta_{\text{O}} = 0.67 \text{ ML}$  as determined by LEED<sup>24</sup> and by comparison with the O(KLL)/Mo(LMM) Auger ratio of an oxygen overlayer deposited by  $\text{CH}_3\text{OH}$  corresponding to 0.35 ML.<sup>25</sup>

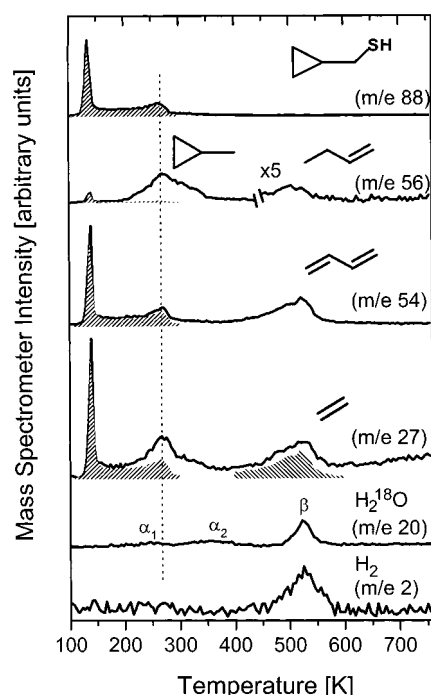
The second chamber contains a Physical Electronics 5300 X-ray photoelectron spectroscopy system. The spectrometer is equipped with a dual Mg/Al X-ray source and a hemispherical electron analyzer. The data reported here were taken using the Mg anode (photon energy of 1253.6 eV). Typically, the photoelectron spectra of four elements, C(1s), Mo(3d), O(1s), and S(2p), are recorded during a single experiment. The Mo(3d) region is monitored for a collection time of 2 min, whereas all others are collected for 8 min. Temperature-annealed X-ray photoelectron data are collected after exposing the oxygen-covered Mo(110) crystal ( $\Theta_{\text{O}} = 0.67 \text{ ML}$ ) to cyclopropylmethanethiol at a crystal temperature of 100 K, annealing at a heating rate of  $\sim$ 10 K/s and recooling to 130 K before data collection. Experiments are independently performed for each temperature. There are no changes in the X-ray photoelectron spectra over time for the collection times used, indicating minimal beam damage to surface species. The Mo(3d<sub>5/2</sub>) peak at 227.8 eV<sup>26</sup> is used to calibrate binding energies of the C(1s), O(1s), and S(2p) regions. Because of spin–orbit coupling in the S(2p) final state, every chemical state of sulfur is associated with two photoelectron peaks. The S(2p<sub>1/2</sub>) and S(2p<sub>3/2</sub>) peaks are separated by 1.2 eV and have a relative intensity of ca. 1:1.8.<sup>27</sup> For data analysis, background intensities are subtracted using spectra recorded for the clean Mo(110) crystal. To improve the signal-to-noise ratio, three data sets are averaged for all temperatures above 200 K. The spectra are fitted with pure Gaussian functions using Microcal Origin (version 4.1) with full-width at half-maximum values typically between 1 and 1.4 eV.

Cyclopropylmethanethiol is prepared on a small scale by the generalized procedure of Cossair et al.<sup>28</sup> A mixture of 0.50 g (3.50 mmol) of triethylene glycol and 0.309 g (4.07 mmol) of thiourea are mixed in a 25 mL flask fitted with a magnetic stirrer, thermometer, dropping funnel, and a short-path distillation apparatus. The temperature of the mixture is brought to 55 °C, and 0.5 g (3.70 mmol) of bromomethylcyclopropane is added through the addition funnel. The flask temperature is increased to 65 °C upon addition of the bromide. Afterward, the reaction temperature is further increased to 90 °C and maintained for 15 min. Tetraethylenepentamine (0.70 g, 3.7 mmol) is added to the mixture through the addition funnel, resulting in an increase in the flask temperature to 97 °C. The product is fractionally distilled and collected as a colorless liquid, bp 62–65 °C. <sup>1</sup>H NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  0.16–0.20 (m,

TABLE 1: Results of Temperature-Programmed Reaction Spectrometry

	<i>m/e</i>										
	88	56	55	54	53	47	41	39	29	28	27
Mass Fragmentation Patterns of Authentic Samples											
(C <sub>3</sub> H <sub>5</sub> )CH <sub>2</sub> –SH <sup>a</sup>	12	14	63	65	27	43	38	100	53	133	118
methylcyclopropane <sup>b</sup>		52	25	11	14		100	77	32	45	76
1-butene		42	23	3	7		100	53	18	45	42
1,3-butadiene			3	68	48			100	1	41	68
ethene									4	100	58
Experimental Mass Fragmentation Patterns for Sample of Methylcyclopropanethiol on O-Modified Mo(110) (Θ <sub>O</sub> = 0.67 ML)											
multilayer <sup>c</sup>	65	7	100	60	31	67	17	70	55	34 <sup>d</sup>	79
molecular layer <sup>e</sup>	23	63	60	34	24	31	100	92	42	17 <sup>d</sup>	94
products <sup>f</sup> (160–400 K)		64	25	13	14		100	71	25	5 <sup>d</sup>	70
products <sup>g</sup> (400–600 K)		10	10	55	42		29	100	10	22 <sup>d</sup>	98
mixture of 1-butene/1,3-butadiene/ethene (20:65:15)		11	9	59	43		26	100	6	67	81

<sup>a</sup> Gas-phase background mass spectrum. <sup>b</sup> Obtained from reaction of methylcyclopropane thiol on clean Mo(110) (data not shown). <sup>c</sup> Integrated over multilayer peak at 145 K. <sup>d</sup> This peak lacks some intensity because of CO-background correction. <sup>e</sup> Integrated peak areas in the 160–400 K temperature range. <sup>f</sup> Intensity left after subtraction of molecular layer using the *m/e* 88 peak intensity as scaling factor. <sup>g</sup> Integrated over the product peak at 400–620 K.



**Figure 1.** Temperature-programmed reaction spectra obtained after condensing multilayers of cyclopropylmethanethiol on <sup>18</sup>O-covered Mo(110) (Θ<sub>O</sub> = 0.67 ML). The traces for ions representative of cyclopropylmethanethiol (*m/e* = 88), methylcyclopropane (*m/e* = 56), 1-butene (*m/e* = 56), 1,3-butadiene (*m/e* = 54), ethene (*m/e* = 27), H<sub>2</sub><sup>18</sup>O (*m/e* = 20), and dihydrogen (*m/e* = 2) are shown. A constant heating rate of 10 ± 2 K/s is used between 100 and 760 K. The dashed line highlights the temperature (270 K) of maximum desorption for the molecular layer. The shaded areas represent contributions from fragmentation (see text).

2H), 0.53–0.57 (m, 2H), 0.98–1.05 (m, 1H), 1.43 (t, *J* = 7 Hz, 1H), 2.43 (t, *J* = 7 Hz, 2H). The <sup>1</sup>H NMR data are in good agreement with previously reported spectra.<sup>29</sup> <sup>13</sup>C NMR (CDCl<sub>3</sub>, 400 MHz) gives δ 5.71, 15.03, 30.29. Gas-phase infrared bands are observed at 1168(w), 1249(m), 2944(s), 3014(s), and 3089(s) cm<sup>−1</sup>.<sup>30</sup> The cyclopropylmethanethiol is stored in a glass bottle over molecular sieves and freeze–pumped–thawed several times at the beginning of each experimental day.

Oxygen (O<sub>2</sub>, 99.998% Matheson), dihydrogen sulfide (H<sub>2</sub>S, Matheson), D<sub>2</sub> (99.7% *d*, Matheson), and <sup>18</sup>O<sub>2</sub> (95–98% isotopic purity, Cambridge Isotope Labs) are used as received. CD<sub>3</sub>–CD<sub>2</sub>OD (ethanol-*d*<sub>6</sub>, 98% *d*, Cambridge Isotope Labs) and D<sub>2</sub>O

(99.96% *d*, Aldrich) are also stored in glass bottles. Ethanol-*d*<sub>6</sub> is stored over molecular sieves. The purity of all substances is routinely confirmed by mass spectrometry.

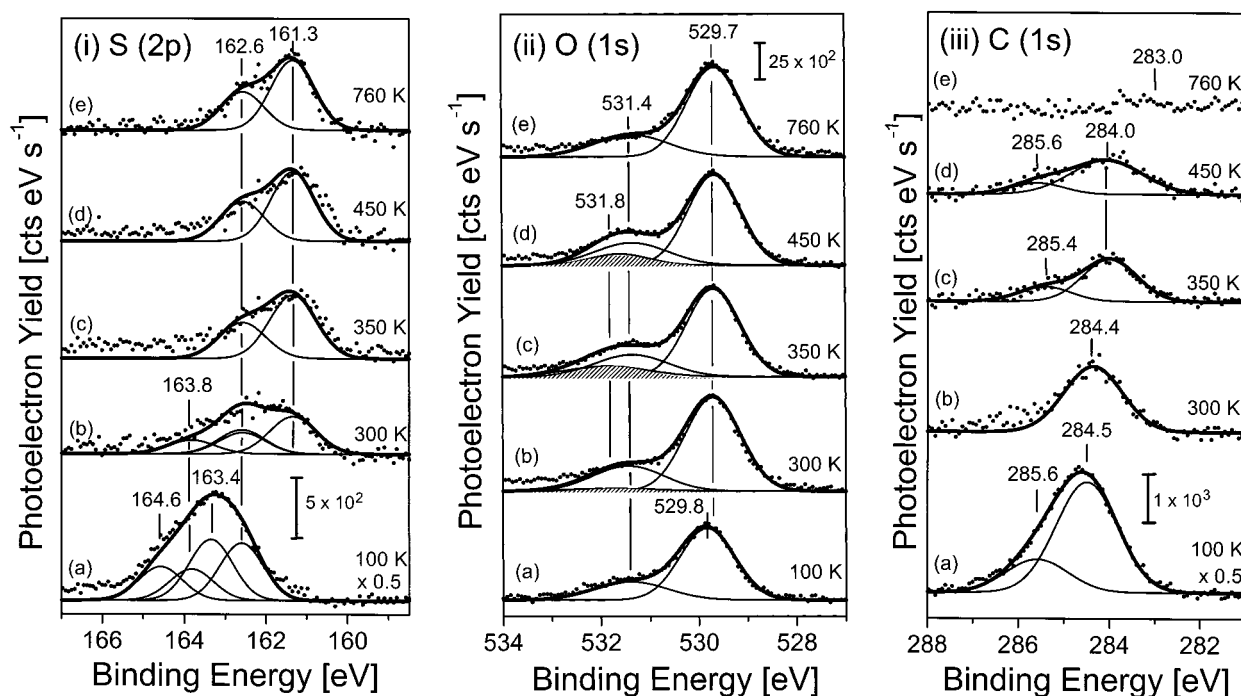
## Results

**Temperature-Programmed Reaction.** Cyclic and linear hydrocarbon species evolve near 300 and 500 K, respectively, during temperature-programmed reaction of cyclopropylmethanethiol multilayers condensed onto oxygen-covered Mo(110) (Θ<sub>O</sub> = 0.67 ML) (Figure 1). The 300 K feature is attributed to methylcyclopropane, whereas the open-chain products 1,3-butadiene, 1-butene, and ethene are formed in the peak near 500 K. Quantitative comparison of the mass spectrometric data with fragmentation patterns measured for the most intense masses of authentic samples yields a 1-butene/1,3-butadiene/ethene ratio of 20:65:15 for the 500 K peak (Table 1). This ratio is in reasonable agreement with the 22:60:18 ratio reported for the oxygen analogue hydroxymethylcyclopropane.<sup>15</sup>

Sublimation of intact cyclopropylmethanethiol is observed in a sharp peak at 145 K (Figure 1). The peak appears for high exposures of cyclopropylmethanethiol and increases indefinitely with exposure, indicating desorption from multilayers. Molecular desorption is detected at ~270 K in conjunction with product formation. This peak reaches maximum intensity for a dosing time of 60 s and stays constant thereafter.

The 300 K peak is identified as the hydrogenation product methylcyclopropane by comparison with earlier studies of cyclopropylmethanethiol on clean Mo(110).<sup>29</sup> On clean Mo(110), efficient C–S bond cleavage and abstraction of adsorbed hydrogen lead to formation of methylcyclopropane (75%)<sup>31</sup> over a broad temperature range from ~200 to 400 K. Note that on oxygen-covered Mo(110), methylcyclopropane production overlaps with the temperature range where the intact thiol desorbs from the molecular layer at 270 K (Figure 1). However, the difference in peak shape of the *m/e* 56 trace compared to that of the parent ion, C<sub>4</sub>H<sub>7</sub>SH (*m/e* 88), and the intensity remaining after correction for parent mass fragmentation (shaded areas in Figure 1, Table 1) clearly indicate that a separate product is formed. Intermolecular reaction of cyclopropylmethanethiol molecules can be excluded as the origin of methylcyclopropane formation because methylcyclopropane is also observed at coverages less than a molecular layer (data not shown). The methylcyclopropane desorption peak at 300 K saturates before a saturation coverage of cyclopropylmethanethiol is reached and the peak maximum shifts to slightly lower temperatures with





**Figure 2.** (i) S(2p), (ii) O(1s), and (iii) C(1s) X-ray photoelectron spectra of (a) cyclopropylmethanethiol multilayers and cyclopropylmethanethiol monolayer heated to (b) 300, (c) 350, (d) 450, and (e) 760 K on oxygen-covered Mo(110). The tail to higher binding energy observed in the O(1s) spectra is attributed to final-state effects, which asymmetrically broaden core peaks on the high binding energy side.<sup>59</sup> Shaded areas in part ii indicate additional O(1s) intensity (see text).

increasing coverage, whereas the 500 K peak saturates with saturation coverage. Integration of the 300 and 500 K product peaks of trace *m/e* 39 (after correction for fragment contributions, Table 1)<sup>32,33</sup> yields a methylcyclopropane to linear C<sub>4</sub> hydrocarbon branching ratio of 35:65.

Experiments in which cyclopropylmethanethiol is coadsorbed with D<sub>2</sub>, ethanol-*d*<sub>6</sub>, or D<sub>2</sub>O indicate that surface hydroxyl groups donate hydrogen en route to methylcyclopropane formation in the 200–350 K region. There is no detectable incorporation of D into any of the hydrocarbon products when the oxygen-covered Mo(110) surface is exposed to a saturation dose of D<sub>2</sub> prior to cyclopropylmethanethiol adsorption. D<sub>2</sub> desorbs intact over a temperature range from 350 to 450 K; however, no D<sub>2</sub>O or HDO is formed. These results suggest that OD<sub>a</sub> is *not* formed from D<sub>2</sub> adsorption on O-covered Mo(110). In contrast, deuterium is incorporated into the 300 K product when cyclopropylmethanethiol reacts on a surface precovered with hydroxyl groups, OD<sub>a</sub>. The OD<sub>a</sub> groups are prepared by exposure of the oxygen overlayer to either ethanol-*d*<sub>6</sub> or D<sub>2</sub>O using coverages lower than saturation. Adsorption of either molecule leads to O–D bond cleavage and OD<sub>a</sub> group formation with surface oxygen.<sup>34,35</sup> Note that ethanol-*d*<sub>6</sub> leads to formation of OD<sub>a</sub> and ethoxy-*d*<sub>5</sub> groups. A single deuterium is incorporated into the methylcyclopropane; methylcyclopropane-*d*<sub>1</sub> accounts for 28 and 15% of the yield when reaction occurs in the presence of OD<sub>a</sub> formed from D<sub>2</sub>O and ethanol-*d*<sub>6</sub>, respectively. The different yields are attributed to different coverages of OD<sub>a</sub>. The maximum of the methylcyclopropane peak at 300 K is shifted ~15 K higher in temperature when OD<sub>a</sub> is prepared from D<sub>2</sub>O.

Removal of surface oxygen is indicated by detection of isotopically labeled water (H<sub>2</sub><sup>18</sup>O, *m/e* 20) in temperature-programmed reaction of cyclopropylmethanethiol on <sup>18</sup>O-covered Mo(110). Water desorption peaks near 250, 350, and 530 K are designated as α<sub>1</sub>, α<sub>2</sub>, and β, respectively.

No gaseous sulfur-containing species, i.e., S<sub>2</sub>, SH, H<sub>2</sub>S, SO<sub>x</sub>, and SO<sub>x</sub>H<sub>y</sub> are detected during temperature-programmed reaction

between 300 and 760 K, in good agreement with the pronounced S(LMM) signal found in the Auger spectrum obtained following temperature-programmed reaction to 760 K. Since all sulfur left on the surface after annealing to 760 K must originate from the thiol, the saturation coverage can be determined by comparison with Auger intensities from overlayers with known sulfur coverages. Thus, the saturation coverage of cyclopropylmethanethiol on oxygen-covered Mo(110) is estimated to be 0.2 ML by comparison with the S(LMM) Auger intensity of a saturated 0.5 ML S overlayer on clean Mo(110).<sup>34</sup> There is no carbon detected by Auger spectroscopy on the surface obtained after heating to 760 K and no H<sub>2</sub> desorption above background levels in temperature-programmed reaction data. Dihydrogen desorbs in a single peak at 530 K (Figure 1). The H<sub>2</sub> peak can be entirely attributed to background H<sub>2</sub>. Consistent with this assertion is the fact that the H<sub>2</sub> intensity is invariant with cyclopropylmethanethiol exposure. Further, no high-temperature CO formation is observed, clearly indicating that no nonselective decomposition of cyclopropylmethanethiol occurs.

**X-ray Photoelectron Spectroscopy.** X-ray photoelectron data obtained following adsorption of cyclopropylmethanethiol on oxygen-covered Mo(110) (Θ<sub>O</sub> = 0.67 ML) are consistent with formation of methylcyclopropane thiolate at 100 K. The S(2p) region is used to distinguish the thiolate from the intact thiol. S(2p) photoelectron data obtained for condensed multilayers (Figure 2ia) are best fit with two sets of doublets separated by 0.8 eV corresponding to intact thiol with S(2p<sub>1/2</sub>) and S(2p<sub>3/2</sub>) binding energies of 164.6 and 163.4 eV, respectively, and surface-bound thiolate at 163.8 and 162.6 eV (Table 2). These binding energies are identical to those measured for 2-methyl-2-propanethiol.<sup>36</sup> The ratio of thiol to thiolate is nearly 1:1, indicating that a substantial amount of S–H bond cleavage occurs at 100 K.

Carbon–sulfur bond cleavage commences at temperatures as low as 200 K. The S(2p) peak broadens after heating to 200 K to lower binding energies due to formation of adsorbed sulfur

**TABLE 2: Summary of X-ray Photoelectron Binding Energies and Curve-Fitting Parameters for Cyclopropylmethanethiol on O–Mo(110)**

		S(2p)				C(1s)		O(1s)		
		2p <sub>1/2</sub>	2p <sub>3/2</sub>	2p <sub>1/2</sub>	2p <sub>3/2</sub>					
100 K	binding energy (eV)	164.6	163.4	163.8	162.6	285.6	284.5	531.4 <sup>a</sup>	529.8	
thiol, thiolate, and	area (counts eV/s)	750	1362	697	1282	2593	7715	2320	6750	
atomic O	peak width (eV)	1.06	1.06	1.06	1.06	1.26	1.26	1.5	1.12	
300 K	binding energy (eV)	163.8	162.6	162.6	161.3	284.4		531.8	531.4 <sup>a</sup>	529.7
thiolate, atomic S	area (counts eV/s)	165	290	256	450	2252		462	3100	8990
and O, and alkoxide	peak width (eV)	1.14	1.14	1.14	1.14	1.28		2.0	1.5	1.14
350 K	binding energy (eV)	162.6	161.3			285.4	284.0	531.9	531.4 <sup>a</sup>	529.7
atomic S and O	area (counts eV/s)	431	762			451	1356	1531	2799	8108
and alkoxide	peak width (eV)	1.14	1.14			1.14	1.20	1.7	1.5	1.08
450 K	binding energy (eV)	162.6	161.3			285.6	284.1	531.6	531.4 <sup>a</sup>	529.7
atomic S and O	area (counts eV/s)	440	774			345	1466	1144	2824	8179
and alkoxide	peak width (eV)	1.06	1.06			1.14	1.59	1.2	1.5	1.08
760 K	binding energy (eV)	162.6	161.3					531.4 <sup>a</sup>	529.7	
atomic S and O	area (counts eV/s)	427	779					2846	8313	
	peak width (eV)	1.06	1.06					1.5	1.12	
reference <sup>b</sup>	binding energy (eV)	162.6	161.3					531.4 <sup>a</sup>	529.8	
atomic S and O	area (counts eV/s)	1104	1756					3472	10114	
	peak width (eV)	0.9	0.9					1.5	1.12	

<sup>a</sup> Satellite peak (see text). <sup>b</sup> Reference for Mo(110)–p(4 × 1)-S and Mo(110)–(6 × 1)-O surfaces.

(S<sub>a</sub>), which has S(2p<sub>1/2</sub>) and S(2p<sub>3/2</sub>) binding energies of 162.6 and 161.3 eV, respectively (data not shown). The evidence for C–S bond cleavage at 200 K obtained with X-ray photoelectron spectroscopy agrees with the onset of methylcyclopropane formation (*m/e* 56) in temperature-programmed reaction (Figure 1). The reduction of the S(2p) peak intensity by ~60% upon heating to 200 K is attributed to multilayer desorption at ~140 K (Figure 1).

Further heating leads to additional C–S bond dissociation. The S<sub>thiol</sub>/thiolate ratio is 3:2 (Figure 2ib) after heating to 300 K and intact thiol is no longer detected on the surface, in good agreement with completion of molecular desorption near 270 K (Figure 1) and a further reduction of the S(2p) intensity by 10%.

Only atomic sulfur with binding energies at 162.6 and 161.3 eV is detected after heating to 350 K (Figure 2ic), indicating completion of C–S bond cleavage. The S(2p) intensity and peak positions are the same after heating to 350, 450, and 760 K, in agreement with temperature-programmed reaction data. There is no evidence for S–O bond formation, which would shift the S(2p) binding energies by more than 3.5 eV to higher binding energies based on adsorption studies of SO<sub>2</sub> on Mo(110).<sup>37</sup> The amount of sulfur deposited corresponds to the saturation coverage of cyclopropylmethanethiol and is estimated to be 0.2 ML, based on the 1:2.4 ratio of S(2p) intensities relative to the Mo(110)–p(4 × 1)-S overlayer (Θ<sub>S</sub> = 0.5 ML, Table 2).

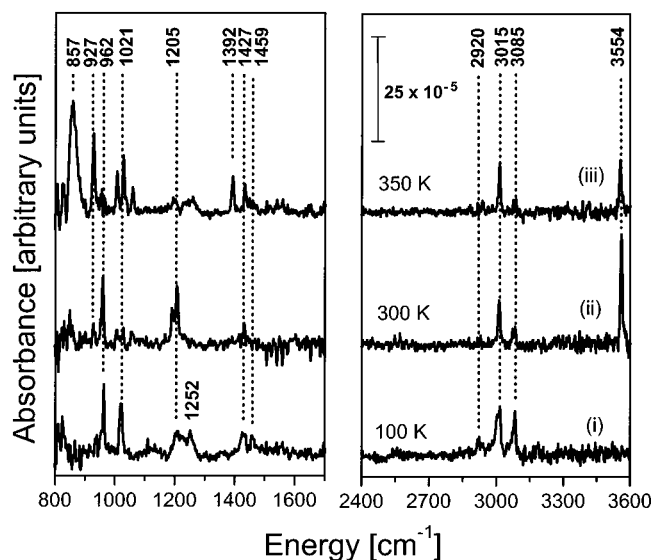
X-ray photoelectron data obtained for the C(1s) and O(1s) regions are generally consistent with formation of C–O bonds as C–S bond dissociation proceeds (parts ii and iii of Figure 2). In the O(1s) region, there is a residual intensity best fit by a peak at 531.8 eV (shaded areas in Figure 2ii). Atomic oxygen has a binding energy of 529.8 eV, while the residual intensity is in the region expected for alkoxides on oxygen-precovered Mo(110).<sup>35,38</sup> At 350 K, for example, this peak is ~20% of the intensity of the atomic oxygen peak at 529.8 eV. Unfortunately, the presence of the satellite peak at 531.4 eV<sup>39</sup> for atomic oxygen precludes a detailed quantitative analysis. Quantitative analysis is further hampered by the presence of OH groups on the surface (see below), which have a binding energy of ~531.8 eV.<sup>35</sup> However, the O(1s) X-ray photoelectron spectrum obtained for hydroxymethylcyclopropane after heating to 350 K

shows a distinct peak at 531.9 eV (data not shown), in good agreement with the assignment of intensity in this region to the ring-closed alkoxide species.<sup>40</sup> Retention of the signal at ~531.8 eV is observed upon annealing of the surface to 450 K (Figure 2iid) despite removal of OH<sub>a</sub> as α<sub>2</sub>-H<sub>2</sub>O observed at 350 K in temperature-programmed reaction (Figure 1). Therefore, we assign this oxygen to the ring-opened alkoxide species. Good agreement is again observed when the data are compared to the O(1s) X-ray photoelectron spectra of 3-buten-1-ol and hydroxymethylcyclopropane heated to 450 K (data not shown).<sup>40</sup> The residual intensity at 531.8 eV disappears upon heating to 760 K, corresponding to hydrocarbon and β-H<sub>2</sub>O elimination in temperature-programmed reaction. The O(1s) intensity detected at 760 K corresponds to a residual oxygen coverage of ~0.55 ML. The changes in the O(1s) spectra are highly reproducible; hence, the intensity at ~531.8 eV attributed to the alkoxide formation is *not* an artifact.

The spectra of the C(1s) region (Figure 2iii) also have residual intensity at a binding energy consistent with formation of an alkoxide. Multilayers of cyclopropylmethanethiol show a broad, asymmetric peak (Figure 2iiia), which is fit best with two curves centered at 285.6 and 284.5 eV with relative intensities of 1:3. The high binding energy peak is assigned to the carbon bound to sulfur (C<sub>s</sub>), whereas the other three carbon atoms in the ring (C<sub>r</sub>) lead to the 284.5 eV signal. The binding energy for C<sub>s</sub> is right between those measured for 2-methyl-2-propanethiol and thiolate, 285.8 and 285.4 eV, respectively,<sup>36</sup> indicating the presence of a mixture of thiol and thiolate in the cyclopropylmethanethiol system. This observation is in excellent agreement with the two chemical states observed for sulfur (see above). The low binding energy peak at 284.5 eV is slightly above (~0.3 eV) those found for other thiols studied on clean Mo(110).<sup>36,41–43</sup> The 300 K C(1s) spectrum is dominated by a peak centered at 284.4 eV with a small high binding energy shoulder. C(1s) binding energies of ~284 eV have been assigned to alkyl fragments adsorbed on clean Mo(110).<sup>36,41,44</sup> Therefore, we assign this peak to methylcyclopropane trapped on the surface, in good agreement with maximum methylcyclopropane formation at 300 K observed in temperature-programmed reaction (Figure 1). The high binding energy shoulder is attributed to both residual C–S bonds and newly formed C–O bonds. An

**TABLE 3: Vibrational Assignment ( $\text{cm}^{-1}$ ) for Selected Infrared Modes of Cyclopropylmethanethiol and -thiolate on Clean and O-Modified Mo(110)**

mode	Mo(110)		Mo(110)-(6 × 1)-O	
	(C <sub>3</sub> H <sub>5</sub> )CH <sub>2</sub> -SH <sup>a</sup>	<i>c</i> -C <sub>3</sub> H <sub>5</sub> -CH <sub>2</sub> S- <sup>a</sup>	(C <sub>3</sub> H <sub>5</sub> )CH <sub>2</sub> -SH <sup>b</sup>	<i>c</i> -C <sub>3</sub> H <sub>5</sub> -CH <sub>2</sub> S- <sup>b</sup>
$\nu(\text{C}-\text{C})$	938	958	958	962
$\nu(\text{C}-\text{S})^b$	1015	1012	1019	1016
$\nu(\text{C}-\text{C})_{\text{ring}}$	1048, 1256, 1304	1195	1046, 1252	1207
CH <sub>2</sub> scissor	1422	1430	1457	1463
$\nu(\text{S}-\text{H})$	2530			
$\nu(\text{C}-\text{H})$	2865, 2915, 2981, 2992, 3069	2904, 2999, 3075	2920, 3003, 3017, 3083	2904, 3019, 3070, 3080

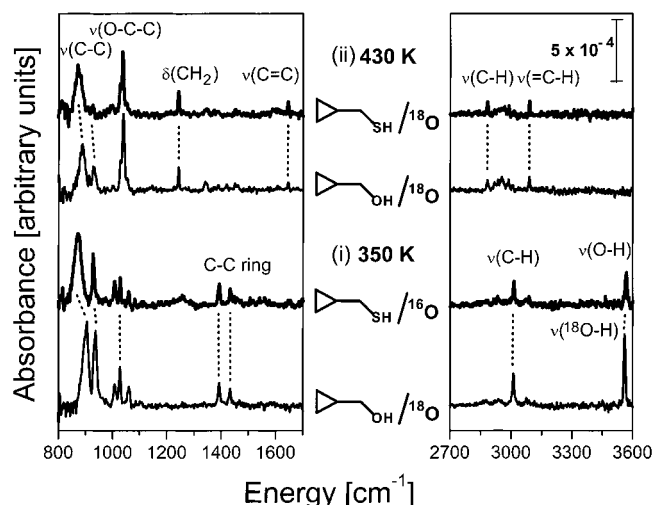
<sup>a</sup> Taken from ref 29. <sup>b</sup> This study.**Figure 3.** Reflection absorption infrared spectra of (i) condensed cyclopropylmethanethiol multilayers on <sup>18</sup>O-modified Mo(110) ( $\Theta_{\text{O}} = 0.67$  ML) and after heating of the sample in part i to (ii) 300 and (iii) 350 K, employing a heating rate of  $10 \pm 2$  K/s.

asymmetric peak, which is fit with curves centered at binding energies of  $\sim 285.5$  and  $284.0$  eV, is apparent after heating to 350 and 450 K. Note that the peak separation between low and high binding energy carbon has increased from 0.9 to  $\sim 1.5$  eV compared to the 100 K spectrum. The  $\sim 1.5$  eV energy difference between the peaks is consistent with that expected for molecules containing C–O bonds.<sup>45</sup> The low S/N ratio precludes detailed analysis; however, the binding energy is consistent with alkoxide formation and compares well with C(1s) X-ray photoelectron data obtained for the ring-closed and linear alkoxides (not shown).<sup>40</sup> Notably, no C(1s) signal remains after heating to 760 K.

Quantitative analysis of the overall intensity changes in the S(2p) and C(1s) peak areas (Table 2) between 200 and 350 K yields a methylcyclopropane to linear hydrocarbon branching ratio of 40:60, which is in reasonable agreement with the 35:65 ratio obtained from temperature-programmed reaction.

**Fourier Transform Infrared Spectroscopy.** Fourier transform infrared data provide evidence for low-temperature transfer of the intact methylcyclopropyl unit from sulfur to oxygen *without* rearrangement (Figure 3). Subsequent ring opening of the cyclic alkoxide to the linear alkoxide and alkyl species occurs in the temperature range from 350 to 430 K based on comparison with infrared spectra of the O analogue hydroxymethylcyclopropane (Figure 4). All infrared results are consistent with the conclusions drawn from X-ray photoelectron and temperature-programmed reaction data.

Infrared data confirm that a mixture of cyclopropylmethanethiol and thiolate is formed upon adsorption of multilayers of

**Figure 4.** Comparison of infrared data obtained after adsorption of cyclopropylmethanethiol (upper trace) and hydroxymethylcyclopropane multilayers (lower trace) on O-modified Mo(110) ( $\Theta_{\text{O}} = 0.67$  ML) after heating to (i) 350 K (note upper trace is cyclopropylmethanethiol on <sup>16</sup>O) and (ii) 430 K.

cyclopropylmethanethiol onto O-covered Mo(110). Residual intensities at 958 and  $1046 \text{ cm}^{-1}$  as well as the peak at  $1252 \text{ cm}^{-1}$  are assigned to the presence of some intact thiol by comparison to infrared data obtained from cyclopropylmethanethiol adsorption on the clean Mo(110) surface (Table 3).<sup>29</sup> Note that the  $\nu(\text{S}-\text{H})$  stretch may not be observed because of orientation effects, which might render this dipole forbidden.<sup>29</sup> Annealing to 200 K (data not shown) removes the multilayer thiol; concomitantly, the peaks at 958, 1046, and  $1252 \text{ cm}^{-1}$  disappear, indicating that they arise from the thiol.

Infrared data also indicate that C–S bonds break and that isolated surface OH<sub>a</sub> groups form after heating to 300 K. There is a dramatic decrease in the intensity of the  $1019 \text{ cm}^{-1}$  peak accompanied by an increase of the  $1205 \text{ cm}^{-1}$  intensity (Figure 3ii), while the relative intensities of all other bands remain almost constant. This is the temperature range where C–S bond dissociation and methylcyclopropane formation occur based on X-ray photoelectron data (see above). Similarly, the  $1015 \text{ cm}^{-1}$  band disappears upon heating of cyclopropylmethanethiol on clean Mo(110) from 200 to 300 K, a temperature where C–S bond cleavage is  $\sim 75\%$  completed based on S(2p) X-ray photoemission data (not shown). The sharp  $\nu(\text{OH})$  peak at  $3554 \text{ cm}^{-1}$  (Figure 3ii, Table 4) signifies the formation of isolated OH groups from H transfer to adsorbed oxygen. The shift in  $\nu(\text{O}-\text{H})$  from  $3554$  for the <sup>18</sup>O-labeled surface to  $3568 \text{ cm}^{-1}$  upon <sup>16</sup>O-labeling confirms this assignment.

Changes in the infrared spectrum upon heating to 350 K provide evidence that the *intact* *c*-C<sub>3</sub>H<sub>7</sub>CH<sub>2</sub> group is transferred from sulfur to oxygen. Specifically, the modes at 857, 927, and  $1028 \text{ cm}^{-1}$  suggest C–O bond formation, whereas the two peaks



**TABLE 4: Vibrational Assignment for Selected Infrared Modes on Oxygen-Covered Mo(110) ( $\Theta_{\text{O}} = 0.67 \text{ ML}$ )<sup>a</sup>**

mode	c-C <sub>3</sub> H <sub>5</sub> –CH <sub>2</sub> <sup>16</sup> O– <sup>a</sup> (cm <sup>−1</sup> )	C <sub>4</sub> H <sub>7</sub> <sup>18</sup> O– <sup>b</sup> (cm <sup>−1</sup> )	C <sub>4</sub> H <sub>7</sub> – <sup>b</sup> (cm <sup>−1</sup> )	H <sup>18</sup> O– <sup>b</sup> (cm <sup>−1</sup> )
$\nu(\text{C–O–Mo})$	905, 936	854, 939		
$\nu(\text{C–O})$	1029	1039		
$\nu(\text{C–C})_{\text{ring}}$			1042	
$\delta(\text{CH}_2)$			1243	
CH <sub>2</sub> scissor	1393, 1434			
$\nu(\text{C=C})$		1645		
$\nu(\text{C–H})$	3018	2936, 3090 <sup>c</sup>	2883, 2958, 2983	
$\nu(\text{O–H})$				3555

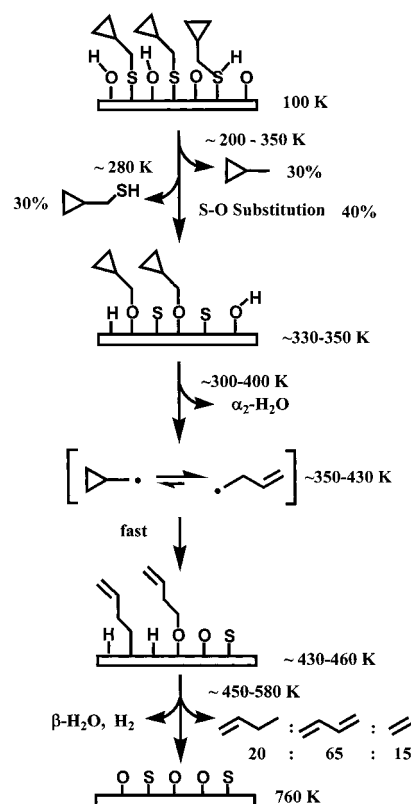
<sup>a</sup> IR data taken from ref 15 for cyclic alkoxide formed from c-C<sub>3</sub>H<sub>7</sub>CH<sub>2</sub>OH on <sup>18</sup>O-covered Mo(110). <sup>b</sup> IR data taken from ref 15 for linear alkoxide species formed from c-C<sub>3</sub>H<sub>7</sub>CH<sub>2</sub>OH on <sup>18</sup>O-covered Mo(110). <sup>c</sup> This stretch has been attributed to a vinylic C–H bond.<sup>58</sup>

near 1400 cm<sup>−1</sup> are attributed to ring modes, indicating that the methylcyclopropoxide species is formed (Figure 3).<sup>46,47</sup> Comparison of the 350 K spectra obtained after heating c-C<sub>3</sub>H<sub>7</sub>CH<sub>2</sub>SH on a <sup>16</sup>O-modified Mo(110) and c-C<sub>3</sub>H<sub>7</sub>CH<sub>2</sub>OH on an <sup>18</sup>O overlayer shows that the spectra are essentially identical (Figure 4i). However, while the number of peaks in both traces is the same, the position of the bands at 905 and 936 cm<sup>−1</sup> appear shifted by 32 and 10 cm<sup>−1</sup>, respectively, to lower wavenumbers in the spectrum obtained from the thiol. Note that the shift of  $\nu(\text{O–H})$  from 3554 to 3568 in Figure 4i is due to the different oxygen isotopes used for the overlayers.

Isotopic labeling of the oxygen layers provides further evidence that transfer of the alkyl unit from sulfur to oxygen takes place below 350 K (data not shown), consistent with X-ray photoelectron data. There are no differences in the spectra obtained for the <sup>16</sup>O- and <sup>18</sup>O-labeled surfaces after annealing of cyclopropylmethanethiol to 250 K, in good agreement with the absence of C–O bond formation below 300 K. In contrast, there are isotopic shifts after heating of both surfaces to 350 K. The 857 cm<sup>−1</sup> peak is ca. 14 cm<sup>−1</sup> higher in frequency on the <sup>16</sup>O overlayer. Closer inspection of this peak reveals that not all intensity is shifted; i.e., integration of the peaks shows that the peak area is ca. 30% smaller on the <sup>18</sup>O overlayer. Similar observations have been made for bromomethylcyclopropane on O-covered Mo(110)<sup>48</sup> and were attributed to partial  $\nu(\text{C–C})$  and  $\nu(\text{C–O})$  character of this infrared band. There might also be a shift in the 1030 cm<sup>−1</sup> region; however, the resolution is not sufficient to resolve this shift.

On the basis of changes in the infrared spectrum (Figure 4ii, Table 4), we conclude that ring opening, yielding the 3-butenoxy species, occurs upon heating to 430 K. The  $\nu(\text{C=C})$  mode at 1645 cm<sup>−1</sup> and the vinylic  $\nu(\text{C–H})$  peak at 3089 cm<sup>−1</sup> signify the butenoxy species.<sup>15,16</sup> Comparison with the hydroxymethylcyclopropane system reveals that the changes observed in the infrared spectrum after heating to 430 K are again essentially the same (Figure 4ii).<sup>15</sup> The two peaks in the 800–950 cm<sup>−1</sup> region are much less shifted (16 and 5 cm<sup>−1</sup>) compared to the 350 K spectra. Similar shifts are observed for the bromomethylcyclopropane system, indicating site blocking by deposited sulfur and bromine atoms as the origin for the shifts.

Heating of the surface to 460 K (data not shown) leads to a reduction of the number of peaks in the infrared spectrum compared to the 430 K spectrum, indicating the presence of more than one adsorbate at 430 K. The high-energy shoulder of the broad 871 cm<sup>−1</sup> peak disappears as well as the peaks at 1242 and 2883 cm<sup>−1</sup>. Further, the 1035 cm<sup>−1</sup> peak is shifted by 14 cm<sup>−1</sup> to 1027 cm<sup>−1</sup>. These peaks have previously been assigned to the metal-bound alkyl species (Table 4).<sup>15,16</sup> The

**SCHEME 2**

460 K infrared spectrum agrees well with the spectrum of 3-buten-1-ol heated to 460 K.<sup>15</sup> Comparison of the 460 K spectra obtained with the <sup>16</sup>O- and <sup>18</sup>O-labeled surfaces shows isotopic shifts in the 800–900 and 1025 cm<sup>−1</sup> regions, confirming that the ring-opened species is trapped by surface oxygen but not by sulfur. No shifts due to <sup>18</sup>O labeling are observed above 1100 cm<sup>−1</sup> for all temperatures investigated.

**Discussion**

The reaction of cyclopropylmethanethiol on oxygen-covered Mo(110) provides insight into the residence time of alkyl radical species on a surface and the effect of coadsorbed species on residence times and on the reaction selectivity. Specifically, the presence of coadsorbed sulfur and hydroxyl groups affects nonselective decomposition and hydrogenation pathways. Our work shows that the methylcyclopropyl group of cyclopropylmethanethiol is transferred to oxygen on Mo(110) *without* rearrangement (Scheme 2). We propose that the alkyl group shifts from sulfur to oxygen via transient formation of the methylcyclopropyl radical after homolytic C–S bond cleavage in the cyclic thiolate between 200 and 350 K. Rearrangement does not occur because the rate of rearrangement is slow relative to hydrogenation and transfer to oxygen in this temperature range. Following methylcyclopropoxide formation near 350 K, the process observed is identical to that for hydroxymethylcyclopropane and bromomethylcyclopropane reaction on O-covered Mo(110)<sup>16</sup> except that no nonselective decomposition is observed in the thiol case. All results are consistent with the reaction mechanism depicted in Scheme 2. The reaction scenario can be divided into four stages: (i) S–H bond cleavage upon adsorption, (ii) desulfurization/oxidation at low temperature (~275 K), (iii) radical rearrangement near 400 K, and (iv) high-temperature reductive and  $\beta$ -hydrogen elimination (~500 K). Each of the four stages will be discussed in more detail with respect to mechanistic aspects and time scales in the following text.

**S–H Bond Cleavage.** Cyclopropylmethane thiolate and surface hydroxyl groups are formed upon adsorption of  $c\text{-C}_3\text{H}_7\text{-CH}_2\text{SH}$  onto oxygen-covered Mo(110). The two doublets in the S(2p) X-ray photoelectron region (Figure 2ia) and the 100 K infrared spectrum of condensed cyclopropylmethanethiol multilayers provide clear evidence for thiolate formation (Figure 3i). However, formation of  $\text{OH}_a$  via S–H bond cleavage at low temperatures (<300 K) is not obvious from the data but is proven by observation of water formation when  $\text{H}_2\text{S}$  is reacted with the oxygen overlayer (data not shown). Multi- and molecular-layer desorption of  $\text{H}_2\text{S}$  occurs at 146 and 177 K, respectively. Formation of  $\text{H}_2\text{O}$  is observed in one sharp and one broad desorption peak at  $\sim 240$  and 350 K corresponding to molecular and recombinative desorption of  $\text{H}_2\text{O}$ .<sup>35</sup> X-ray photoelectron data of the O(1s) region confirm that surface OH groups are present at temperatures as low as 100 K and show that  $\sim 10\%$  of the oxygen overlayer is removed as  $\text{H}_2\text{O}$  upon annealing to 500 K. Thus, we conclude that the thiol reacts via S–H bond cleavage to form thiolate and  $\text{OH}_a$  when adsorbed on O-covered Mo(110).

**Desulfurization/Oxidation.** Carbon–sulfur bond dissociation commences at 200 K, the onset of methylcyclopropane formation in temperature-programmed reaction (Figure 1). Near 300 K, three processes compete: (i) C–S bond cleavage accompanied by hydrogenation, yielding gaseous methylcyclopropane; (ii) transfer of the methylcyclopropyl unit from sulfur to oxygen, resulting in the ring-closed methylcyclopropoxide; (iii) molecular desorption of cyclopropylmethanethiol.

We propose that cleavage of the C–S bond at 200 K is *homolytic* in methylcyclopropane thiolate, yielding the methylcyclopropyl radical based on several observations. First, both methylcyclopropane and methylcyclopropoxide form in a similar temperature range. In addition, methylcyclopropane evolves in the same temperature range with a similar peak shape from reaction on both the clean and the oxygen-modified surfaces. The only difference is that about twice as much methylcyclopropane per cleaved C–S bond is formed on the clean surface (data not shown). Further, methylcyclopropane is formed from  $c\text{-C}_3\text{H}_7\text{CH}_2\text{OH}$  reaction beginning near 400 K on clean Mo(110) (data not shown), which is 200 K higher than methylcyclopropane formation from the thiol. Previously, a correlation between C–S bond energy and temperature for hydrocarbon elimination was established for several thiolates on clean Mo(110), providing evidence for homolytic C–S bond cleavage.<sup>9</sup> A similar correlation can be made for C–S and C–O bonds, i.e., C–S bonds in linear thiols are generally  $\sim 20\%$  weaker than the C–O bond in the corresponding alcohols.<sup>49</sup> Thus, the 200 K higher temperature of methylcyclopropane formation from  $c\text{-C}_3\text{H}_7\text{CH}_2\text{OH}$  compared to  $c\text{-C}_3\text{H}_7\text{CH}_2\text{SH}$  supports the postulation of homolytic C–S bond cleavage. The higher temperature for product evolution from  $c\text{-C}_3\text{H}_7\text{CH}_2\text{OH}$  also excludes the ring-closed alkoxide as the intermediate en route to methylcyclopropane formation below 350 K on O-covered Mo(110). Notably, there is no detectable methylcyclopropane formation from reaction of  $c\text{-C}_3\text{H}_7\text{CH}_2\text{OH}$  on oxygen-modified Mo(110).<sup>15</sup>

Metal-bound alkyls and thiocarboxylates are unlikely to be intermediates. Insertion of molybdenum into the C–S bond leading to a metal-bound alkyl species is eliminated as a source for methylcyclopropane formation, based on the absence of methylcyclopropane evolution when bromomethylcyclopropane is reacted on oxygen-covered Mo(110), where partial formation of a metal-bound alkyl near 200 K is indicated by  $\delta(\text{CH}_2) = 1242\text{ cm}^{-1}$ .<sup>16</sup> Formation of a thiocarboxylate intermediate, i.e.,

oxidative addition, is ruled out on the basis of the absence of  $d_2$ -incorporation in  $\text{D}_2$ ,  $\text{D}_2\text{O}$ , and ethanol- $d_6$  coadsorption experiments because it would require C–H bond cleavage upon O addition followed by double hydrogenation, i.e.,  $d_2$ -incorporation, eliminating both sulfur and oxygen concomitantly at 200 K.

Thus, we conclude that *homolytic* C–S bond cleavage yields the methylcyclopropyl radical at 200 K, which abstracts hydrogen from surface hydroxyl groups to form methylcyclopropane as indicated by formation of methylcyclopropane- $d_1$  on the OD-precovered surface. The lack of reaction with  $\text{D}_a$  on O-covered Mo(110) is surprising because methylcyclopropane- $d_1$  evolution (55%) is observed when cyclopropylmethanethiol is adsorbed onto D-precovered Mo(110).<sup>29</sup> We attribute the absence of  $d_1$ -incorporation from  $\text{D}_a$  on O-covered Mo(110) to reduced mobility of surface H(D) caused by the blocking of hydrogen adsorption sites by surface oxygen. This effect has been measured for H adsorbed on oxygen-covered W(110).<sup>50</sup> Clearly, this is an example where the presence of other adsorbed species dramatically effects reactivity.

The absence of 1-butene and 1,3-butadiene formation indicates that rearrangement of the methylcyclopropyl radical to the linear butenyl radical (Scheme 1) is too slow at 200 K to compete efficiently with hydrogen abstraction from adsorbed  $\text{OH}_a$ , i.e.,  $k_{\text{hydrogenation}}(200\text{ K}) > k_{\text{rearrange}}(200\text{ K})$ . Assuming that the rate constants of rearrangement in solution and on the surface are similar,<sup>51</sup> the rate constant for rearrangement at 200 K is calculated as  $k_{\text{rearrange}}(200\text{ K}) = 2.5 \times 10^6\text{ s}^{-1}$  corresponding to a characteristic reaction time of 4  $\mu\text{s}$ , based on the  $T$ -dependent expression of the rate constant published by Halgren et al.<sup>17</sup>

Trapping of the methylcyclopropyl radical by surface oxygen competes effectively with hydrogenation between 300 and 350 K. Methylcyclopropane formation peaks at 270 K and decreases continuously until it stops at 350 K despite the fact that isolated OH groups are still present on the surface as indicated by the residual  $3554\text{ cm}^{-1}$  peak in the infrared spectrum taken after heating to 350 K (Figure 3iii). This is in contrast to the almost constant methylcyclopropane formation commencing at 260 K and its abrupt decrease above 350 K because of  $\text{H}_2$  recombinative desorption on the clean surface.<sup>29</sup> The small amount of  $\alpha_2$ -water desorption *cannot* account for the decaying methylcyclopropane production on oxygen-covered Mo(110). Thus, we attribute the decrease in methylcyclopropane formation to a more effective competition of radical trapping by surface oxygen as the temperature increases. Infrared data obtained at 350 K (Figure 4) and the correspondence in hydrocarbon production temperatures and yields in temperature-programmed reaction provide convincing evidence to the assertion that methylcyclopropoxide is formed. Since no rearrangement occurs, as indicated by the absence of the  $1645\text{ cm}^{-1}$  stretch in the infrared, we are able to place a lower bound on the rate constant for radical trapping, namely,  $k_{\text{trap}}(350\text{ K}) > k_{\text{rearrange}}(350\text{ K}) = 4.73 \times 10^8\text{ s}^{-1}$  (2.1 ns).

The efficient competition of trapping with hydrogenation above 300 K is attributed to the change in the number of available exposed oxygen atoms that serve as trapping sites. To a first approximation, assuming that the effect of the sulfur deposited by C–S bond cleavage is negligible, the reaction rates for methylcyclopropane and methylcyclopropoxide formation can be expressed as second-order processes:





The two rate constants  $k$  and  $k'$  depend on the barrier heights for reaction and the diffusion of methylcyclopropyl radical, O<sub>a</sub>, and OH<sub>a</sub> on the surface. Both reactions are likely to be exothermic and barrier-free because the methylcyclopropyl radical is quenched in the course of the reaction and such processes are generally barrier-free in gas-phase reactions; therefore,  $k$  and  $k'$  are mainly determined by the difference of OH<sub>a</sub> and O<sub>a</sub> diffusion on Mo(110). The latter is described by  $D_0(\text{O}_a) = 1 \times 10^{-3} \text{ cm}^2 \text{ s}^{-1}$  and  $E_{a,\text{diff}}(\text{O}) = 82 \text{ kJ/mol}$ ,<sup>52</sup> which gives  $D_0(300 \text{ K}) = 6.4 \times 10^{-18} \text{ cm}^2 \text{ s}^{-1}$  (about one Mo atom per second on the Mo(110) plane); thus, O diffusion is negligible compared to trapping and hydrogenation, which have to be faster than  $k_{\text{rearrange}}(300 \text{ K}) = 8.85 \times 10^7 \text{ s}^{-1}$  (11 ns) because no rearrangement is observed. Therefore, we assume that  $k$  and  $k'$  have the same order of magnitude and similar  $T$  dependencies, reducing the difference in  $R(\text{c-C}_3\text{H}_5\text{CH}_3)$  and  $R'(\text{OCH}_2\text{-c-C}_3\text{H}_5)$  to the relative amounts of OH<sub>a</sub> groups and free O<sub>a</sub> surface sites. Thus, the ratio  $R'(\text{OCH}_2\text{-c-C}_3\text{H}_5)/R(\text{c-C}_3\text{H}_5\text{CH}_3)$  is approximately equal to the  $\Theta_{\text{O}}/\Theta_{\text{OH}}$  ratio. Assuming that the amount of oxygen removed as  $\alpha_1$ -water in the 300 K region is negligible, the sum  $K$  of OH<sub>a</sub> and O<sub>a</sub> is constant and given by the oxygen overlayer concentration:

$$\frac{R(\text{OCH}_2\text{-c-C}_3\text{H}_5)}{R'(\text{c-C}_3\text{H}_5\text{CH}_3)} \approx \frac{\Theta_{\text{O}_a}}{\Theta_{\text{OH}_a}} = \frac{K}{\Theta_{\text{OH}_a}} - 1 \quad (3)$$

At 200 K methylcyclopropane formation starts to deplete OH<sub>a</sub>, thereby reducing  $\Theta_{\text{OH}_a}$  and increasing  $K/\Theta_{\text{OH}_a}$ . As a result, the  $R'(\text{OCH}_2\text{-c-C}_3\text{H}_5)/R(\text{c-C}_3\text{H}_5\text{CH}_3)$  ratio constantly increases; i.e., more methylcyclopropyl radicals are trapped by surface oxygen and less c-C<sub>3</sub>H<sub>7</sub>CH<sub>3</sub> is formed. Desorption of molecularly adsorbed cyclopropylmethanethiol near 270 K leads to an additional increase of free oxygen sites O<sub>a</sub>, again favoring trapping of the radical.

**Radical Rearrangement.** The methylcyclopropyl-butenyl radical rearrangement (Scheme 1) occurs between 350 and 430 K in a process similar to that previously reported for hydroxymethylcyclopropane.<sup>15</sup> The appearance of vibrational bands characteristic of the linear butenoxide, i.e.,  $\nu(\text{C}=\text{C}) = 1645 \text{ cm}^{-1}$ , and the vinylic  $\nu(\text{C}=\text{H}) = 3080 \text{ cm}^{-1}$  is clear evidence for rearrangement (Figure 4, Table 4). Once the radical is formed, it rearranges to the butenyl radical, which is then trapped by surface oxygen and exposed molybdenum atoms. According to Halgren's<sup>17</sup>  $T$ -dependent rate constant expression for this rearrangement,  $k_{\text{rearrange}}$  spans from  $4.73 \times 10^8$  to  $30.6 \times 10^8 \text{ s}^{-1}$  (from 2.1 to 0.3 ns) in the 350–430 K range, leading to a lower limit of 2.1 ns for the residence time,  $t_{\text{res}}$ , of the C<sub>4</sub>H<sub>7</sub> radical on O-covered Mo(110) and an upper limit for  $k_{\text{trap}} < k_{\text{rearrange}} = 30.6 \times 10^8 \text{ s}^{-1}$ . The absence of any reductive or  $\beta$ -hydrogen elimination yielding ring-closed or linear C<sub>4</sub> hydrocarbons in temperature-programmed reaction indicates that rearrangement and trapping of the rearranged radical by surface oxygen are faster than hydrogenation in the 350–430 K temperature range, i.e.,  $k_{\text{hydrogenation}}(350 \text{ K}) < k_{\text{rearrange}}(350 \text{ K}) = 4.73 \times 10^8 \text{ s}^{-1}$ .

Stair et al.<sup>53</sup> recently investigated the residence time of CH<sub>3</sub> radicals on a MgO(100) surface, employing a time-of-flight mass spectrometer. An Arrhenius analysis of the residence times provides a desorption barrier of  $E_a = 2.5 \pm 0.5 \text{ kcal mol}^{-1}$  and a preexponential factor of  $\nu = 10^{10 \pm 1} \text{ s}^{-1}$ . By use of the  $E_a$  and  $\nu$  values, residence times of 4–2 ns are calculated for temperatures of 350 and 430 K. Although MgO(100) and oxygen-covered Mo(110) are very different surfaces, we assume that the activation energy and preexponential factor characterizing

this weak interaction can be generally applied because the residence time was measured only for thermally desorbed methyl radicals.<sup>53</sup> The calculated residence times agree favorably with the lower limit of  $t_{\text{res}} \geq 2.1 \text{ ns}$  at 350 K required for the radical to rearrange.

**High-Temperature Elimination.** Above 430 K product desorption sets in. Hydrogen abstraction leads to 1-butene formation, whereas  $\beta$ -hydrogen elimination results in 1,3-butadiene. A small amount of C–C bond cleavage leads to ethene formation. Desorption of  $\beta$ -H<sub>2</sub>O occurs concomitantly with 1,3-butadiene desorption, indicating that high-temperature water formation involves the alkoxide oxygen. Furthermore, no deuterium incorporation into 1-butene and  $\beta$ -H<sub>2</sub>O is observed when cyclopropylmethanethiol is adsorbed onto an OD-precovered surface, clearly showing that OH<sub>a</sub> groups are not involved in high-temperature hydrogenation and  $\beta$ -water formation. 1-Butene, 1,3-butadiene, and ethene are formed in a 20:65:15 ratio, which agrees nicely with the 22:60:18 ratio observed for reaction of c-C<sub>3</sub>H<sub>7</sub>CH<sub>2</sub>OH on O-covered Mo(110).<sup>15</sup>

**Effect of Sulfur.** Sulfur does not affect the temperature for ring opening or C–O bond cleavage. It does, however, influence reaction selectivity by completely suppressing the nonselective decomposition, an effect most likely due to site blocking. A similar site-blocking effect can be mimicked when hydroxymethylcyclopropane is adsorbed onto an oxygen-covered Mo(110) surface precovered with  $\sim 0.2 \text{ ML}$  of sulfur.<sup>40</sup> Crowding or site blocking may also be the rationale for absence of radical trapping by exposed Mo atoms, which has been observed at temperatures as low as 200 K in the bromomethylcyclopropane/O/Mo(110) system.<sup>16</sup>

## Conclusion

Adsorption of cyclopropylmethanethiol onto oxygen-modified Mo(110) leads to formation of a thiolate species and a surface hydroxyl group via S–H bond cleavage at temperatures as low as 100 K. Homolytic C–S bond cleavage commences at 200 K, the onset of methylcyclopropane formation, and is completed by 350 K. Transfer of the intact methylcyclopropyl unit from sulfur to oxygen competes efficiently with hydrogenation of methylcyclopropane between 300 and 350 K. The number of available exposed oxygen atoms that serves as trapping sites is identified as the origin of this competition. Once the methylcyclopropoxide is formed, the observed reactivity very much resembles that observed for the alkoxides formed from bromomethylcyclopropane and hydroxymethylcyclopropane; however, the residual sulfur present on the surface completely suppresses the nonselective decomposition pathway.

Assuming that the rate constant for rearrangement on the surface is similar to that in solution, limits are estimated for the rate constants for hydrogenation and trapping:  $k_{\text{hydrogenation}}(200 \text{ K}) > 2.5 \times 10^6 \text{ s}^{-1}$ ,  $k_{\text{hydrogenation}}(350 \text{ K}) < 4.73 \times 10^8 \text{ s}^{-1}$ ,  $k_{\text{trap}}(350 \text{ K}) > 4.73 \times 10^8 \text{ s}^{-1}$ , and  $k_{\text{trap}}(430 \text{ K}) < 30.7 \times 10^8 \text{ s}^{-1}$ , using Halgren's<sup>17</sup> definition for the rearrangement constant.

Comparing the reactivity of cyclopropylmethanethiol on clean and O-covered Mo(110) shows that modification of the surface with oxygen reduces the desulfurization pathway; i.e., the pathway of hydrogenation yielding methylcyclopropane is decreased by 35% to 40%. The other 60% is directed into C–O bond formation, yielding alkoxide species on the surface, which then later undergo isomerization to the linear species.

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- (31) The other pathway observed on the clean surface is nonselective decomposition. C(1s) and S(2p) X-ray photoelectron data obtained for a multilayer coverage of cyclopropylmethanethiol heated to 200 and 760 K are used to estimate the branching between methylcyclopropane formation and nonselective decomposition to 3:1.
- (32) A similar detection efficiency of our mass spectrometer is assumed for methylcyclopropane, 1-butene, and 1,3-butadiene based on the very similar sensitivity factors of ca.  $1.3 \times 10^{-3}$ .<sup>33</sup>
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