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Probing the Kinetics for Thiol Desulfurization: The Reactions of 2-Methyl-2-propanethiol on Mo(110)

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The reactions of 2-methyl-2-propanethiol on Mo(110) were studied using temperature programmed reaction, high resolution electron energy loss, and X-ray photoelectron spectroscopies. The sulfur–hydrogen bond breaks upon adsorption at 120 K, yielding adsorbed 2-methyl-2-propyl thiolate and hydrogen. Thiolate hydrogenolysis produces isobutane, while cleavage of the C–S and selective C–H bond breaking β to the sulfur yields isobutene. Nonselective decomposition to adsorbed carbon, sulfur, and gaseous dihydrogen is a competing channel. At reaction saturation, the selectivity for hydrocarbon formation is 80%. The specific butane and butene isomers were identified on the basis of the differences in the fragmentation patterns of the various isomers when an electron energy of 27 eV was used in the mass spectrometer. The isomeric selectivity corroborates our general mechanism for thiolate reaction. Isobutane formation preceded ethane formation for a 2-methyl-2-propanethiol/ethanethiol mixture. The kinetics for 2-methyl-2-propyl thiolate desulfurization were found to increase with increasing 2-methyl-2-propyl thiolate coverage.

Introduction

The reactions of sulfur-containing molecules on single crystal surfaces have been the subject of intense investigation, motivated by an interest in metal-catalyzed desulfurization. A general mechanism for the desulfurization of organic thiols on Mo(110) has been proposed from our earlier work. To date, the C_1–C_5 primary thiols[1-5] and benzenethiol[6,7] have been investigated on an initially clean Mo(110).

Briefly, S–H bond cleavage occurs upon adsorption at 120 K, forming the corresponding thiolate (RS–) on the surface. In the case of the primary thiolates, C–S bond hydrogenolysis yields the corresponding alkanes, while competing C–S bond breaking and dehydrogenation at the 2-carbon produces the respective alkenes. Analogously, gaseous benzene and adsorbed benzyne are formed during the desulfurization of adsorbed phenyl thiolate.[6,7] In all cases, the selectivity for hydrocarbon production over nonselective decomposition increases at high thiolate coverages.

Our earlier studies suggested that the rate limiting step for thiolate hydrogenolysis involved C–S bond breaking. We have previously shown that the kinetics for C–S bond hydrogenolysis of the primary thiolates are *independent* of alkyl chain length.[8] All alkanes are formed with essentially the same kinetics during temperature programmed reaction of a mixture of ethane-, 1-propane-, 1-butane-, and 1-pentanethiol.[8] The hydrogenolysis kinetics for the phenyl thiolate, however, are slower than the primary thiolates. For example, ethane is formed faster than benzene during temperature programmed reaction of a mixture of benzenethiol and ethanethiol. Since the coadsorption of the thiolates ensure identical conditions for the reaction intermediates, these experiments are indicative of *intrinsic* differences in the hydrogenolysis kinetics of primary thiolates and phenyl thiolate. The observed differences in kinetics correlate with the homolytic C–S bond strengths of the thiolates[9] and also with the stability of the alkyl radicals proposed to be formed from C–S bond cleavage.[10]

This study was undertaken to test the hypothesis that the rate limiting step for thiolate hydrogenolysis on Mo(110) has a large component of C–S bond scission by studying a branched thiol. On the basis of the reaction scheme formulated for linear thiols, we predict that isobutane and isobutene should be formed from the reaction of 2-methyl-2-propanethiol on Mo(110). Indeed, these are the observed products, and the ability to identify the specific alkane and alkene isomers was essential in testing our mechanism.

Furthermore, 2-methyl-2-propyl thiolate is expected to react more rapidly than the primary thiolates based on relative strengths: 68.4 kcal/mol for the C–S bond in 2-methyl-2-propanethiol versus 72.2 kcal/mol[9] for that in ethanethiol. As predicted, 2-methyl-2-propanethiol produces isobutane with more rapid kinetics than ethane is formed from ethyl thiolate.

Experimental Section

All experiments were performed in three separate ultrahigh vacuum chambers, described in detail previously.[4,11,12] The working base pressure in these chambers was always $\leq 2 \times 10^{-10}$ Torr. The details of the temperature programmed reaction, high resolution electron energy loss, and X-ray photoelectron experiments have also been described elsewhere.[12,13]

Briefly, the electron energy loss chamber was equipped with a computer-controlled LK2000-14-R electron spectrometer. The spectrometer was operated at a primary electron energy of 3 eV and had a spectral resolution of 55–85 cm^{-1} (7–11 meV). The resolution varied as a result of distinctly different surface reflectivity for monolayer and multilayer coverages. All spectra were collected at the specular angle.

2-Methyl-2-propanethiol (Aldrich, 99%) was dried over sodium sulfate and distilled under an atmosphere of dry nitrogen. Sample purity was confirmed frequently by mass spectrometry during the time the experiments were performed. Before each day's experimentation, the sample was degassed by several freeze–pump–thaw cycles. Dihydrogen (99.9995%), dideuterium (99.0%), hydrogen sulfide (99.5%), dioxygen (99.8%), isobutane (99.5%), *n*-butane (99.5%), *cis*-2-butene (99+%), 1-butene (99.0%), and isobutene (99.0%) were obtained from Matheson and were used without further purification.

The Mo(110) surface was cleaned in an oxygen environment at a crystal temperature of 1200 K before each reaction. The crystal was then flashed to 2000 K, producing a clean surface.

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No carbon, sulfur, or oxygen were detected in Auger electron or X-ray photoelectron experiments performed immediately before 2-methyl-2-propanethiol adsorption. A sharp (1 × 1) LEED pattern was also observed.

Auger electron spectra were used to estimate reaction selectivities and saturation coverages. The C/S Auger ratio, $R_{C/S}$, is defined as the ratio of the peak to peak heights of the following Auger signals:[14]

$$R_{C/S} = \frac{[C(KLL, 272\,eV)]}{[Mo(LMM, 148\,eV)] + [S(KLL, 152\,eV)]}$$

Auger electron spectra collected following thiophene decomposition on Mo(110) were used as reference data for C_4S surface composition. Thiophene decomposes to surface carbon and sulfur and gaseous dihydrogen, on Mo(110), with *no* hydrocarbon evolution.[15,16] $R_{C/S}$ following reaction of a saturation amount of thiophene was 0.15 ± 0.01. The S/Mo Auger ratio, $R_{S/Mo}$, is defined as the ratio of the peak to peak heights measured in the derivative spectra of the following Auger signals:

$$R_{S/Mo} = \frac{[Mo(LMM, 148\,eV)] + [S(KLL, 152\,eV)]}{[Mo(LMM, 186\,eV)] + [Mo(LMM, 221\,eV)]}$$

The Mo(110)-$p(4\times1)$-S surface has a sulfur coverage of Θ_s = 0.50 monolayers and was used as a reference.[17] $R_{S/Mo}$ for the Mo(110)-p(4×1)-S surface is 2.0 ± 0.1.[18]

Temperature programmed reaction data were obtained using electron energies of both 27 and 70 eV in the mass spectrometer. Differences in the fragmentation patterns of the butene and butane isomers are augmented by the 27-eV electron energy and used to identify specific isomers of butane and butene. The fragmentation patterns of authentic samples of the different butene and butane isomers were measured both by back-filling the chamber to a pressure of ~6 × 10^{-10} Torr and by subliming multilayers of the isomers from the Mo(110) crystal. There were no differences in the data obtained using the two different methods. The butane and butene isomers produced during temperature programmed reaction of 2-methyl-2-propanethiol on Mo(110) were identified by comparing the product fragmentation patterns to those for the different hydrocarbon isomers using a 27-eV electron energy. The electron energy was monitored frequently to ensure stability, and an entire set of experiments was performed on the same day to minimize experimental variation.

Results

I. Temperature Programmed Reaction of 2-Methyl-2-propanethiol on Clean Mo(110). Butane, butene, and dihydrogen are produced from 2-methyl-2-propanethiol reaction on Mo(110) (Figure 1). Carbon and sulfur remain on the surface as nonvolatile products. No other products were evolved during the temperature programmed reaction based on a comprehensive search of all masses in the range of 2–90 amu. In particular, no other hydrocarbons or sulfur-containing compounds were detected. All data shown are for the molecular ion, except for butane. In this case, *m/e* 43 was monitored because it is approximately 50 times more intense than the molecular ion (*m/e* 58). Experiments were performed in which the 58:43 ion ratios were measured and were found to be in agreement with those measured for authentic samples of isobutane.

For saturation exposures of 2-methyl-2-propanethiol, butane and butene are formed over a wide range of temperatures, 160–360 K. Saturation exposure is defined as the minimum exposure required for the maximum product yield. The rate of hydrocarbon formation reaches a maximum at 325 and 350 K for isobutane and isobutene, respectively. 2-Methyl-2-propanethiol (*m/e* 90) multilayers sublime at 160 K for exposures greater than saturation.

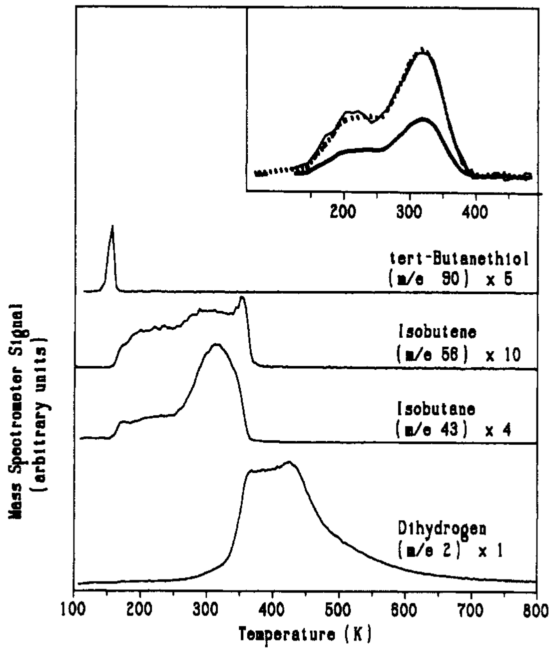

Figure 1. Temperature programmed reaction of 2-methyl-2-propanethiol on Mo(110) at an exposure just exceeding saturation. The masses monitored were dihydrogen (*m/e* 2), isobutene (*m/e* 56), isobutane (*m/e* 43), and 2-methyl-2-propanethiol (*m/e* 90). The spectra are uncorrected for the degree of ionization in the mass spectrometer. The isobutene and isobutane spectra are corrected for 2-methyl-2-propanethiol fragmentation at 160 K. In the inset, the actual *m/e* 43 spectrum for 2-methyl-2-propanethiol on Mo(110) (solid line) is compared to calculated *m/e* 43 spectra derived from the fragmentation patterns of isobutane (dotted line) and *n*-butane (heavy solid line) and the measured *m/e* 42 spectra of 2-methyl-2-propanethiol.

The rates of both butane and butene formation are limited by reaction based on a comparison with the reactions of *n*-butane, isobutane, isobutene, 1-butene, and *cis*-2-butene on Mo(110). The alkanes, isobutane and *n*-butane, molecularly desorbed in a single peak at 160 K. The alkenes desorbed at 160 and 200 K. Nonselective decomposition of the alkenes to atomic carbon and gaseous dihydrogen was also observed. Since the hydrocarbon products mainly evolve above the desorption temperature during 2-methyl-2-propanethiol reaction, the kinetics for their formation are reaction-limited. The onset of hydrocarbon production, however, may have a small component rate-limited by desorption.

Approximately 80% of the 2-methyl-2-propanethiol that reacts on Mo(110) yields hydrocarbons as determined by Auger electron spectra. The remaining ~20% nonselectively decomposes to surface carbon and sulfur and gaseous dihydrogen. The C/S Auger ratio measured following temperature programmed reaction of a saturation exposure of 2-methyl-2-propanethiol on Mo(110) was 0.04 ± 0.01. From the reaction of thiophene on Mo(110), a C_4S species would have a C/S Auger ratio of 0.15. On the basis of this ratio, the stoichiometry following 2-methyl-2-propanethiol reaction is $C_{0.8}S$. Therefore, ~20% of the carbon remains on the surface from nonselective decomposition, while the other 80% is removed by hydrocarbon formation. X-ray photoelectron data yield an estimate of ~85% selectivity for hydrocarbon formation. The C(1s) intensity measured at 160 K represents the amount of *tert*-butyl thiolate available for reaction, and the C(1s) intensity after heating to 800 K corresponds to the amount of carbon produced from nonselective decomposition. The ratio of the C(1s) intensity at 800 K to that at 160 K is ~0.15, which is in reasonable agreement with the estimate of 20% nonselective decomposition obtained from Auger electron data.

The saturation coverage of 2-methyl-2-propanethiol is estimated to be ~0.2 based on the S/Mo Auger ratio. Since no sulfur-containing molecules leave the surface during the reaction, the 2-methyl-2-propyl thiolate coverage is the same as the amount

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[14] Since the S(*KLL*, 152 eV) and Mo(*LMM*, 148 eV) Auger peaks overlap, any reference to the sulfur signal must include the Mo peak at 148 eV. For sulfur coverages greater than 0.1 monolayer, the Mo(*LMM*, 148 eV) peak height is negligible.

[15] Roberts, J. T.; Friend, C. M. *Surf. Sci.* **1987**, *186*, 201.

[16] All Auger spectra were collected after the crystal was cooled to 120 K.

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TABLE I: Fragmentation Patterns for Butene Isomers at 27-eV Ionization Energy

molecule	m/e 41:m/e 56	molecule	m/e 41:m/e 56
1-butene	1.99 ± 0.06	isobutene	1.47 ± 0.04
cis-2-butene	1.29 ± 0.03	butene product	1.55 ± 0.06

of sulfur remaining on the surface after temperature programmed reaction. $R_{S/Mo}$ = 0.8 ± 0.1, compared to 2.0 ± 0.1 for the Mo(110)-p(4×1)-S surface which has a sulfur coverage of 0.50.[18] Similarly, the saturation coverage of 2-methyl-2-propanethiol is estimated to be ~0.2 based on the S(2p) X-ray photoelectron intensities of the Mo(110)-p(4×1)-S surface, Θ_s = 0.50, and the surface after heating a saturation exposure of 2-methyl-2-propanethiol to 800 K.

Isotopic exchange experiments demonstrate that a single C-H(D) bond is formed when butane is produced, while *no* C-H(D) bonds are formed during butene formation. Temperature programmed reaction of 2-methyl-2-propanethiol in the presence of deuterium (saturation dose) produces only butane-d_0 and -d_1. No deuterium is incorporated into the butene product in these experiments; only butene-d_0 is detected.[19] This demonstrates that no reversible C-H(D) activation occurs along the reaction path for hydrocarbon formation. Preadsorption of deuterium also increases the butane yield, without significantly effecting the yield of the butene. Dihydrogen, HD, and D_2 all evolve with similar kinetics over a broad temperature range of 310-550 K in these experiments.

II. Butane and Butene Isomer Determination. Identification of the specific butane and butene isomers formed from the 2-methyl-2-propyl thiolate reaction is important in testing the details of the reaction mechanism. There are two isomers of butane, *n*-butane and isobutane, and five possible butene isomers, 1-, *cis*-2-, and *trans*-2-butane and iso- and cyclobutane. Cyclobutane is easily ruled out as m/e 28 is its most intense fragment, contrary to what is observed during reaction. Unfortunately, there are no significant differences in the fragmentation patterns of the other four butene isomers under standard operating conditions: a 70-eV electron energy.[20] Fortunately, differences in the fragmentation patterns of these isomers are augmented at low electron energy (Figure 1 inset and Table I).

The butane isomer was assigned as isobutane based on the m/e 43:m/e 42 ratio measured for the product of the 2-methyl-2-propanethiol reaction on Mo(110) measured with an electron energy of 27 eV. The $C_3H_7^+$ ion (m/e 43) is produced from loss of a methyl. Additional loss of hydrogen yields the $C_3H_6^+$ ion, m/e 42. There are substantial differences in the m/e 43:m/e 42 ratio for the butane isomers for an electron energy of 27 eV. The measured m/e 43:42 ratios were 2.4 ± 0.1 and 5.4 ± 0.2 for authentic samples of isobutane and *n*-butane, respectively. The m/e 43:m/e 42 ratio was 2.5 ± 0.2 for the butane produced from 2-methyl-2-propyl thiolate hydrogenolysis. The inset in Figure 1 shows the measured m/e 43 profile, along with the m/e 43 profile calculated for *n*-butane and isobutane to illustrate the difference. The m/e 43 and 42 profiles had only a minor contribution to their intensity from the butene product. Accordingly, the butane isomer could be determined independently from the butene product.

Identification of the butene isomer depends upon the butane identity, since both butane and butene produce fragment ions with m/e 41 and 56. The major fragment ion for all isomers of butene is m/e 41, corresponding to the loss of one methyl group. The butene parent ion is m/e 56. Since the butane and butene product peaks overlap in the temperature programmed reaction spectrum (Figure 1), the contributions of isobutane fragmentation to the m/e 41 and 56 signals were substracted by scaling with respect to the 43 amu intensity. On the basis of the resulting m/e 41:m/e 56 ratio of 1.5 in the temperature programmed reaction of 2-methyl-2-propanethiol, isobutene is assigned as the butene product (Table I).

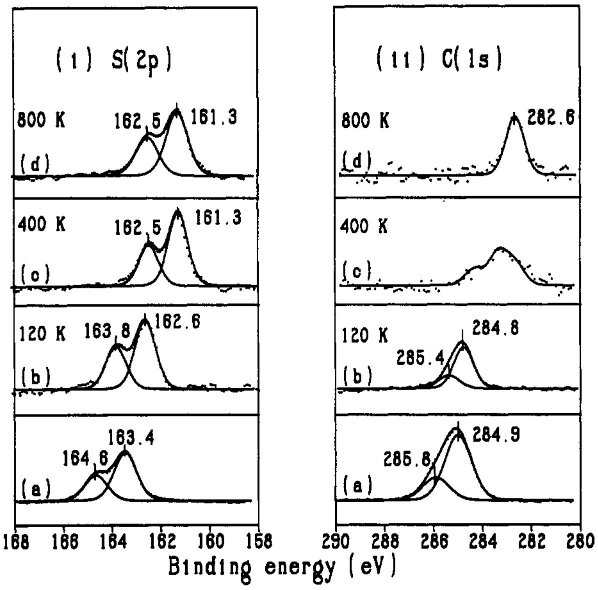

Figure 2. (i) S(2p) and (ii) C(1s) X-ray photoelectron spectra of (a) 2-methyl-2-propanethiol multilayers and a 2-methyl-2-propanethiol monolayer annealed to (b) 120 K, (c) 400 K, and (d) 800 K.

TABLE II: S(2p) and C(1s) X-ray Photoelectron Spectroscopy Data

		$S(2p_{1/2})$	$S(2p_{3/2})$	C(1s)	
100 K	binding energy, eV	164.6	163.4	285.8	284.9
	area, (counts eV)/s	2960	5480	5870	16730
	peak width, eV	1.1	1.1	1.3	1.3
160 K	binding energy, eV	163.8	162.6	285.4	284.8
	area, (counts eV)/s	600	970	625	1850
	peak width, eV	1.0	1.0	1.0	1.0
400 K	binding energy, eV	162.5	161.3		
	area, (counts eV)/s	590	1030	430 (total)	
	peak width, eV	1.0	1.0		
800 K	binding energy, eV	162.5	161.3	282.6	
	area, (counts eV)/s	630	1000	420	
	peak width, eV	1.1	1.1	0.9	

The product identification assumes that the fragmentation patterns of reaction products are the same as the reference data obtained from back-filling of the chamber with authentic samples of the alkene and alkane isomers. Temperature-dependent effects[21] in the fragmentation patterns, while possible, are expected to be minor because the products are formed near 300 K. Furthermore the fragmentation patterns measured for sublimation of multilayers (160 K) of the butane and butene isomers were identical to those for the gas at 300 K, supporting the assertion that the temperature dependence of the ion yields should be minimal. In addition, differences in the fragmentation patterns for 1-butene and *cis*-2-butene are in good agreement with previous reports.[22]

III. X-ray Photoelectron Spectroscopy. C(1s) and S(2p) X-ray photoelectron experiments are consistent with the formation of *tert*-butyl thiolate upon adsorption at 120 K (Figure 2, Table II). S(2p) X-ray photoelectron data provide evidence for a single sulfur-containing species on the surface at 120 K, while the C(1s) data are consistent with a *tert*-butyl skeleton with an intact C-S bond.

X-ray photoelectron data of 2-methyl-2-propanethiol multilayers were obtained as a reference state with $S(2p_{1/2})$ and $S(2p_{3/2})$ binding energies of 164.6 and 163.4 eV, respectively (Figure 2ia), whereas the C(1s) spectrum consists of a broad, asymmetric peak centered at 285.0 eV (Figure 2iia). The C(1s) spectrum is optimally fit with two curves at 285.8 and 284.9 eV, respectively,

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(19) The m/e 57 peak was monitored to check for butene-d_1. The small peak present was due to the natural abundance of ^{13}C in the butene product formed.

(20) *Eight Peak Index of Mass Spectra*; Mass Spectrometry Data Centre, Dyestuffs, Division, Imperial Chemical Industries Ltd.: Reading, PA, 1970; Vol. I, Tables 1 and 2.

(21) Amorebieta, V. T.; Colussi, A. J. *Chem. Phys. Lett.* **1982**, *89*, 193.

(22) Kelly, D. G.; Salmeron, M.; Somorjai, G. A. *Surf. Sci.* **1986**, *175*, 465.

TABLE III: Electron Energy Loss Assignments for 2-Methyl-2-propanethiol[a]

spectral signal, cm^{-1}			
2-methyl-2-propanethiol	2-methyl-2-propyl thioate	gas phase	assignment
2935	2930	2950	ν(C-H)
2525		2565	ν(S-H)
1440	1440	1450	$\delta_a(CH_3)$
nr	1380	1370	$\delta_s(CH_3)$
1180	1180	1180, 1210	ν_a(MeCMe), $\rho(CH_3)$
915	915	930	$\rho(CH_3)$
nr	800	820	ν(C-C)
600	575	587	ν(C-S)
310	376	295	δ(CCS)
310	265	235	$\tau(CH_3)$

[a] nr = not resolved.

with relative intensities of 1:3. The two peaks are assigned to the carbon bonded to sulfur (285.8 eV) and to the other three indistinguishable carbons (284.9 eV).[2]

The C-S bond in 2-methyl-2-propanethiol remains intact based on the $S(2p_{1/2})$ and $S(2p_{3/2})$ binding energies of 163.8 and 162.6 eV measured after adsorption of a saturation dose of 2-methyl-2-propanethiol at 120 K (Figure 2ib). The binding energies are identical to those measured previously for ethyl thiolate and *n*-propyl thiolate on Mo(110) and 1.3 eV higher in energy than atomic sulfur.[2,5] The S(2p) binding energies for Mo(110)-p-(4×1)-S are 162.5 and 161.3 eV.[18] There is no detectable atomic sulfur at this temperature. The C(1s) X-ray photoelectron spectrum is a broad, asymmetric peak, best fit with two peaks at 285.3 and 284.7 eV with relative intensities of 1:3, similar to the multilayer data (Figure 2iib).

Cleavage of the C-S bond of 2-methyl-2-propyl thiolate commences at ~160 K, the onset of butane formation, and is complete by 375 K, based on X-ray photoelectron spectra. In the range of 160-375 K, S(2p) intensity shifts to lower binding energies characteristic of atomic sulfur (162.5 and 161.3 eV). The C(1s) peaks also broaden toward lower binding energies in this temperature range.

All C-S bonds are broken after annealing to 400 K, the temperature where hydrocarbon formation is complete (Figure 2ic). Only two S(2p) peaks at 162.5 and 161.3 eV are observed with peak widths of 1.0 eV. The C(1s) spectrum consists of a broad, asymmetric peak centered at 283.2 eV, with a shoulder at 284.2 eV (Figure 2iic). The C(1s) peaks are attributed to a combination of one or more adsorbed hydrocarbon fragments and adsorbed atomic carbon.[2] The data are not fit since there is not a unique set of peaks. The hydrocarbons remaining on the surface decompose to atomic carbon, sulfur, and gaseous dihydrogen between 400 and 650 K (Figure 1).

IV. High Resolution Electron Energy Loss Spectroscopy. Vibrational data clearly show that the S-H bond is broken upon adsorption in 2-methyl-2-propanethiol to afford 2-methyl-2-propyl thiolate. Electron energy loss spectra of 2-methyl-2-propanethiol multilayers, used as a reference state, contain an S-H stretch at 2525 cm^{-1} as well as losses characteristic of 2-methyl-2-propanethiol (Figure 3a and Table III). The measured losses are in good agreement with gas-phase values; in particular, the S-H stretch is 2570 cm^{-1} in the gas phase.[1,23,24] It is also similar to the ν(S-H) values in other thiols: 2560 cm^{-1} for 2-propanethiol,[25] 2570 cm^{-1} for 2-propene-1-thiol,[26] and 2580 cm^{-1} for benzenethiol.[6]

The absence of the S-H stretch in the spectrum for a 2-methyl-2-propanethiol exposure less than or equal to saturation, taken with the S(2p) photoelectron data, is unequivocal evidence for formation of 2-methyl-2-propyl thiolate (Figure 3b). The remainder of the spectrum is essentially the same as for condensed 2-methyl-2-propanethiol, after taking into account the higher resolution for the monolayer spectrum.[27]

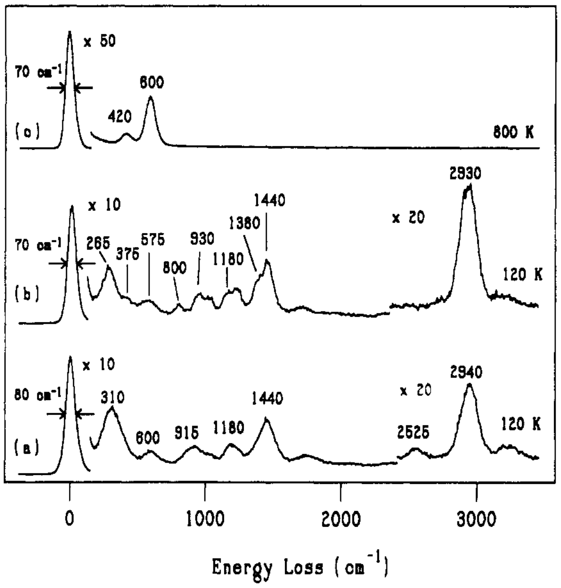

Figure 3. High resolution electron energy loss spectra of (a) 2-methyl-2-propanethiol multilayers at 120 K, (b) 2-methyl-2-propanethiol monolayers at 120 K, and (c) 2-methyl-2-propanethiol multilayers annealed to 800 K.

TABLE IV: Comparison of Skeletal Modes for Isobutane and *tert*-Butyl Thiolate

	energy, cm^{-1}		
mode	gas-phase isobutane	isobutane on Mo(110)	2-methyl-2-propyl thiolate on Mo(110)
ν(C-H)	2960	2940	2930
$\delta_a(CH_3)$	1468	1460	1440
$\delta_s(CH_3)$	1389	1390	1380
$\rho(CH_3)$	1189	1170	1180[a]
$\rho(CH_3)$	913	920	915
ν(C-C)	796	800	800
ν(Mo-C)		570	420, 600
δ(CCC)	367	405	

[a] Contains contributions from the ν_a(MeCMe) mode.

The loss at 2935 cm^{-1} is assigned as the ν(C-H) mode in good agreement with what is observed for gas-phase 2-methyl-2-propanethiol (Figure 3a,b).[1,23,24,28] This loss remains essentially unchanged for the 2-methyl-2-propyl thiolate spectra, indicating that the methyl groups do not interact strongly with the surface.

High resolution electron energy loss spectra of isobutane monolayers (data not shown) are used to determine which modes are due to the sulfur atom and which are due to the hydrocarbon framework (Table IV). Since isobutane and 2-methyl-2-propanethiol have essentially the same hydrocarbon skeleton, modes associated with the skeleton should be similar for the two molecules. As is evident from a comparison of the skeletal modes observed in electron energy loss spectra of isobutane and 2-methyl-2-propyl thiolate, the hydrocarbon framework in 2-methyl-2-propanethiol is not significantly perturbed upon adsorption (Table IV). The losses observed in the electron energy loss spectra are assigned on the basis of gas-phase values for isobutane. There is also a weak loss at 2685 cm^{-1} in the isobutane spectrum which is not well understood, but has been seen pre-

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(24) Scott, D. W.; El-Sabban, M. Z. *J. Mol. Spectrosc.* **1969**, *30*, 317.

(25) Smith, D.; Devlin, J. P.; Scott, D. W. *J. Mol. Spectrosc.* **1968**, *25*, 174.

(26) Wiegand, B. C.; Uvdal, P. E.; Friend, C. M. Manuscript in preparation.

(27) Due to the inherent poorer resolution in the condensed 2-methyl-2-propanethiol electron energy loss spectrum, only the assignment of the broad peaks were made. Some of these broad losses at 915, 1180, and 1440 cm^{-1} are made up of multiple losses, but extensive assignments are not made due to the limited resolution.

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viously in electron energy loss spectra of hydrocarbon intermediates on Mo(110),[26] as well as for isobutane in the gas phase.

The loss at 1440 cm^{-1} is assigned as the $\delta(CH_3)$ mode in agreement with gas-phase values (Figure 3a).[1,23,24,28] The individual asymmetric and symmetric deformation modes cannot be resolved for the multilayer spectrum. However, for the 2-methyl-2-propyl thiolate spectrum, the symmetric deformation mode, $\delta_s(CH_3)$, is partially resolved as a shoulder at ~1380 cm^{-1}, on the low energy side of the asymmetric mode, $\delta_a(CH_3)$ at 1440 cm^{-1}. The magnitude of the splitting of the two modes is similar to that observed for gas-phase 2-methyl-2-propanethiol[23,24,28] and isobutane condensed on Mo(110) (Table IV).

The fact that both the symmetric and asymmetric modes are detected for 2-methyl-2-propyl thiolate indicates that the methyl groups are tilted with respect to the surface[29] and is consistent with a nearly perpendicular C–S bond vector assuming the geometry of the thiolate is essentially the same as the gas-phase thiol. This assumption is supported by the fact that there are only minor differences in the modes associated with the hydrocarbon skeleton for the thiol and thiolate. The somewhat broad losses at 1180 and 915 cm^{-1} in the 2-methyl-2-propanethiol multilayer spectrum are assigned as the ν_a(MeCMe) and $\rho(CH_3)$ modes, respectively (Figure 3a). As seen in the 2-methyl-2-propyl thiolate spectrum, both losses probably consist of at least two different modes (Figure 3b). A more detailed assignment of these peaks is not unambiguous and is therefore not pursued. Both $\rho(CH_3)$ and skeletal deformation modes have been observed in this region in the gas phase.[23,24,28]

A loss at 800 cm^{-1} is also observed in the 2-methyl-2-propyl thiolate spectrum and is assigned as the ν(C–C) mode, again in accordance with gas-phase assignments for 2-methyl-2-propanethiol.[23,24,28] All losses above 700 cm^{-1} are also observed in the electron energy loss spectrum of isobutane on Mo(110), indicating that they are not related to the sulfur atom but rather to the 2-methyl-2-propyl skeleton (Table IV).

The loss at 600 cm^{-1} in the 2-methyl-2-propanethiol multilayer spectrum is assigned as the ν(C–S) mode, in agreement with gas-phase assignments of 2-methyl-2-propanethiol (Figure 3a).[23,24,28,30] This loss is shifted to lower energy, 575 cm^{-1}, in the 2-methyl-2-propyl thiolate spectrum. There is also probably some component of a ν(M–S) mode in the loss at 600 cm^{-1}, which is normally observed in this region,[1] making detailed interpretation difficult.

The loss at 310 cm^{-1} in the 2-methyl-2-propanethiol multilayer spectrum is assigned to the methyl torsion mode, $\tau(CH_3)$, in agreement with gas-phase data (Figure 3a).[24,30] It is shifted down in energy to 265 cm^{-1} for 2-methyl-2-propyl thiolate and has a high energy shoulder at 375 cm^{-1}. This shoulder is tentatively assigned to the δ(CCS) mode in agreement with gas-phase values for 2-propanethiol.[25] This feature has also been seen in gas phase 2-methyl-2-propanethiol spectra but at slightly lower energies.[23] This loss is absent in electron energy loss spectra of isobutane, indicating that it is not related to the hydrocarbon skeleton.

The two losses at ~1700 and 3190 cm^{-1} in Figure 3a are assigned to combination modes of the methyl torsion mode with the $\delta(CH_3)$ and ν(C–H) modes, respectively. The assignment of the two combination modes above 1440 and 2935 cm^{-1} is strengthened by the fact that the methyl torsion mode shifts in energy and is attenuated in the 2-methyl-2-propyl thiolate spectra (Figure 3b), and the proposed combination modes also undergo similar changes.

Electron energy loss spectra show that the modes associated with the 2-methyl-2-propyl thiolate intermediate decrease as the surface is annealed to higher temperatures, while the loss at ~600 cm^{-1} increases in intensity. However, this loss is a combination of ν(C–S), ν(M–S), and ν(M–C) modes, which gives rise to some ambiguities in the interpretation of the increase in intensity. It is, however, consistent with the buildup of atomic sulfur on the surface as hydrocarbons are produced, as corroborated by X-ray photoelectron spectroscopy.

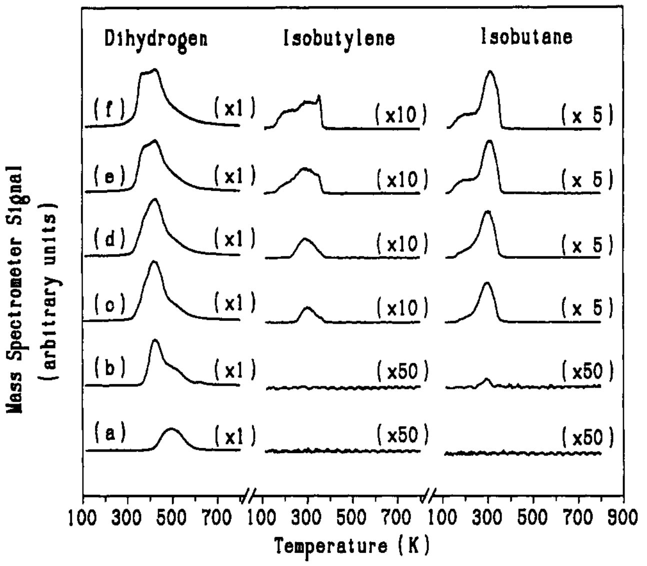

Figure 4. Temperature programmed reaction spectra of 2-methyl-2-propanethiol as a function of 2-methyl-2-propanethiol coverage. The masses monitored were dihydrogen (*m/e* 2), isobutene (*m/e* 56), and isobutane (*m/e* 43). The spectra correspond to (a) 15%, (b) 33%, (c) 50%, (d) 66%, (e) 83%, and (f) 120% of saturation. The data are not corrected for fragmentation.

Electron energy loss spectra indicate that atomic sulfur and carbon remain on the surface after annealing 2-methyl-2-propanethiol to 800 K. There are two losses seen at 420 and 600 cm^{-1}, characteristic of atomic carbon and sulfur on Mo(110).[6]

V. Coverage Dependence of the Reaction of 2-Methyl-2-propanethiol on Clean Mo(110). The selectivity and kinetics for the reaction of 2-methyl-2-propanethiol on Mo(110) are strongly dependent on coverage (Figure 4). At low coverages (<0.20 of saturation), no hydrocarbons are formed, only nonselective, irreversible decomposition to gaseous dihydrogen, *m/e* 2, and surface carbon and sulfur is observed. Dihydrogen desorption is observed in the range of 400–600 K. The C/S ratio derived from Auger data is 4:1, consistent with the lack of volatile hydrocarbon production. For exposures below 0.20 of saturation, $R_{C/S} = 0.16 \pm 0.01$,[15] confirming that only nonselective decomposition occurs.

Isobutane (*m/e* 43) is first observed for an exposure 0.2 of saturation in an asymmetric peak at 300 K. The yield of isobutane increases and the peak becomes more asymmetric as the 2-methyl-2-propanethiol dose increases to saturation. Isobutene (*m/e* 56) is first detected at an exposure 0.33 of saturation. As the exposure time is increased, the isobutane and isobutene peaks increase in area and broaden to lower temperature until the reaction reaches saturation.

The dihydrogen peak also increases with increasing exposure time. At low exposure times, less than 0.2 of saturation, there is a single peak, centered around 490 K. At exposures greater than 0.2 of saturation, a peak centered around 410 K is populated until 0.5 of saturation. Exposure times greater than 0.5 of saturation populate a second dihydrogen peak centered around 360 K. Hydrogen recombination occurs at ~425 K on clean Mo(110), and at ~350 K on Mo(110)–p(4×1)–S. These data suggest that the second H_2 peak at 360 K is due to the deposition of sulfur below this temperature.

Electron energy loss spectra also provide evidence for S–H bond cleavage for all coverages less than or equal to saturation (data not shown). No loss corresponding to the ν(S–H) mode is seen. The rest of the losses, both in energy and relative loss intensity, are essentially the same as those for a saturation exposure of 2-methyl-2-propanethiol.

VI. Coadsorption of a 2-Methyl-2-propanethiol/Ethanethiol Mixture. Temperature programmed reaction of a mixture of 2-methyl-2-propanethiol and ethanethiol shows that the 2-methyl-2-propyl thiolate reacts faster than the primary thiolate,

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(29) Wiegand, B. C.; Uvdal, P. C.; Friend, C. M. Manuscript in preparation.

(30) Scott, D. W.; Crowder, G. A. *J. Mol. Spectrosc.* **1968**, *26*, 477.

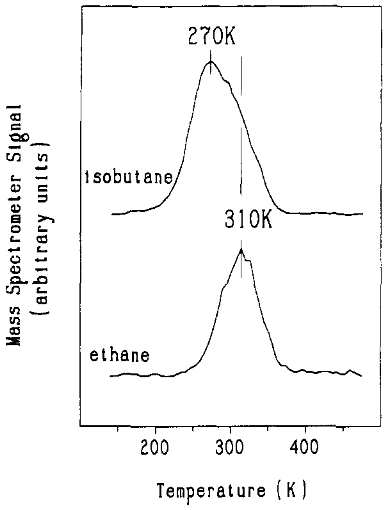

Figure 5. Temperature programmed reaction of a mixture of ethanethiol and 2-methyl-2-propanethiol. The masses monitored were ethane (*m/e* 27) and isobutane (*m/e* 43). The data are uncorrected for fragmentation.

ethyl thiolate (Figure 5). Coadsorption of the two thiols ensures that both thiols react under the same conditions.[31] This is imperative as adsorbed sulfur, hydrogen, and hydrocarbon fragments have been shown to alter the reaction kinetics and selectivity for thiols on Mo(110).[7,13] 2-Methyl-2-propyl thiolate hydrogenolysis proceeds more rapidly than ethyl thiolate hydrogenolysis, based on the differences in peak temperature and the onset of hydrocarbon formation. The peak temperature for isobutane formation from 2-methyl-2-propanethiol is 270 K, compared to 310 K for ethane formation from ethanethiol. Similarly, the onset of isobutane evolution is 200 K, compared to 225 K for ethane. The more rapid reaction of 2-methyl-2-propyl thiolate is consistent with our proposal that C–S bond breaking is the rate limiting step for hydrogenolysis.

Discussion

In accordance with all of our results, we propose the reaction scheme shown in Figure 6 for the desulfurization of 2-methyl-2-propanethiol on Mo(110). This reaction scheme is similar to that proposed earlier for straight chain thiols. 2-Methyl-2-propanethiol adsorbs dissociatively to form adsorbed 2-methyl-2-propyl thiolate and hydrogen at 120 K. X-ray photoelectron and vibrational spectroscopies unequivocally show that the S–H bond is broken, while the C–S bond and the hydrocarbon skeleton remain intact. Hydrogenolysis of the C–S bond to form isobutane competes with dehydrogenation at the 2-carbon to form isobutene in the temperature range of 160–360 K. In a third process, 2-methyl-2-propyl thiolate decomposes to gaseous dihydrogen and adsorbed carbon and sulfur. At reaction saturation, ~80% of the adsorbed 2-methyl-2-propyl thiolates form hydrocarbon products, while ~20% undergo nonselective, irreversible decomposition forming atomic sulfur and carbon with dihydrogen evolution.

Although most vibrational bands in the 2-methyl-2-propyl thiolate spectrum are similar to those of 2-methyl-2-propanethiol, the ν(C–S) loss is lower in energy on the surface: 575 cm^{-1} compared to 600 cm^{-1}. This suggests that there is some C–S bond weakening in 2-methyl-2-propyl thiolate due to adsorption, although it is not substantial. This weakening could facilitate the desulfurization of 2-methyl-2-propanethiol on Mo(110). Weakening of the ν(C–S) mode by ~20–100 cm^{-1} in methanethiol has been seen previously on Fe(100),[32] Cu(100),[33] Ni(110),[34] and Mo(110),[1] where methane was formed via C–S bond scission during the reaction.

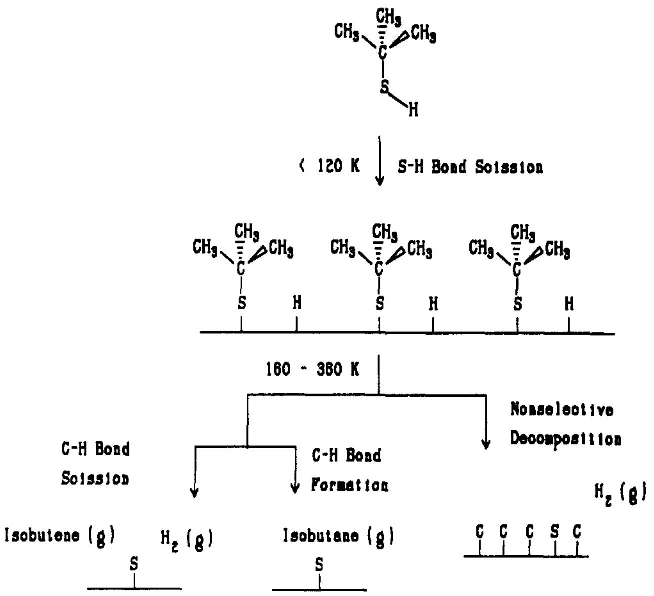

Figure 6. Proposed reaction scheme for 2-methyl-2-propanethiol on Mo(110).

The identification of the specific butane and butene isomers formed during 2-methyl-2-propanethiol desulfurization was essential for testing the general mechanism proposed for straight chain thiols. The formation of isobutane is most direct from hydrogenolysis of the 2-methyl-2-propyl thiolate intermediate, as rearrangement to the primary alkane is thermodynamically unfavorable. The formation of isobutene from the dehydrogenation of the 2-methyl-2-propyl thiolate intermediate at the 2-carbon also agrees with our mechanism. Dehydrogenation at the 2-carbon has been proposed before,[2-4] and this study gives compelling evidence that it actually occurs.

The observation that 2-methyl-2-propyl thiolate reacts more rapidly than ethyl thiolate is consistent with C–S bond scission being the rate limiting step for thiolate hydrogenolysis on Mo(110). The C–S bond is weaker in gaseous 2-methyl-2-propanethiol as compared to ethanethiol: 68.4 kcal/mol vs 72.2 kcal/mol. Therefore, alkane formation from 2-methyl-2-propanethiol should be more rapid than for ethanethiol, if C–S bond scission is rate-limiting and if the trend in C–S bond strengths is the same on the surface as in the gas phase. Indeed, the relative hydrogenolysis kinetics correlate with C–S bond strength. Importantly, spectroscopic and isotopic exchange experiments establish that the reaction mechanism is the same for these two thiols.

The proposed mechanism on Mo(110) is similar to the mechanism for methanethiol on Ni(110), where a surface methyl thiolate intermediate was formed. The thiolate intermediate then underwent C–S bond hydrogenolysis to form gaseous methane.[34] However, it is somewhat different than the mechanism proposed for methanethiol on Fe(100), where C–H bond formation was proposed to be rate-limiting. On Fe(100), Albert and co-workers propose that surface methyl is formed from the reaction of methanethiol. The surface methyl then is hydrogenated to form gaseous methane.[32] However, they do not rule out the presence of a direct hydrogenolysis of a methyl thiolate intermediate. On Cu(100), Sexton and co-workers also propose the formation of surface methyl from the reaction of methanethiol. The surface methyl then recombines with surface hydrogen to form methane.[33]

Our mechanism strongly suggests that C–S bond hydrogenolysis leads to direct production of isobutane and that surface alkyl groups do not lead to hydrocarbon production. If 2-methyl-2-propyl groups were deposited on the surface and C–H bond formation were rate-limiting, as suggested for methanethiol hydrogenolysis on Fe(100), the hydrogenolysis kinetics should not

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[31] The reactant gases were mixed in the dosing line before dosing of the mixture onto the Mo(110) crystal so that the possibility of islanding can be kept to a minimum. However, this can never be completely ruled out.

[32] Albert, M. R.; Lu, J. P.; Bernasek, S. L.; Cameron, S. D.; Gland, J. L. *Surf. Sci.* **1988**, *206*, 348.

[33] Sexton, B. A.; Nyberg, G. L. *Surf. Sci.* **1986**, *165*, 251.

[34] Huntley, D. R. *J. Phys. Chem.* **1989**, *93*, 6156.

correlate with C–S bond strength. Furthermore, alkyl groups are expected to be strongly bound to Mo(110); subsequent rapid and irreversible dehydrogenation of the alkyl is anticipated. Future experiments are planned to better address this point, however.

The isotopic labeling experiments are also in accord with the proposed reaction scheme. Only a single surface deuterium is incorporated into the isobutane product, consistent with the formation of a single C–H(D) bond. Likewise, no deuterium is incorporated into the isobutene product.

The kinetics for hydrocarbon formation are modified by the deposition of sulfur during the course of temperature programmed reaction. We propose that the complex reaction kinetics for hydrocarbon formation reflect the changes in C–S bond activation due to the presence of sulfur. The kinetics for hydrocarbon formation have been previously shown to be dependent upon surface sulfur, carbon, hydrogen, and hydrocarbon fragments.[7,13] Hydrocarbon formation is accompanied by sulfur deposition on the surface and competing nonselective decomposition of the thiolate intermediate produces surface hydrogen, hydrocarbon fragments, and sulfur. Since these processes occur at low temperatures for 2-methyl-2-propanethiol, the reaction kinetics for hydrocarbon formation are being altered by the presence of surface adsorbates on the surface over a wide range of temperatures. More detailed studies of the effect of sulfur are planned.

A possible alternative explanation for the complex kinetics of 2-methyl-2-propanethiol desulfurization could be due to the binding geometry. 2-Methyl-2-propanethiol has been shown to bind in multiple coordination geometries in organometallic complexes.[35–37] In fact, it has been proposed that the reactivity of these different sites would be very different.[35] Since the kinetics for isobutane formation seem to increase with 2-methyl-2-propanethiol coverage and also seem to consist of at least two separate pathways, this is a viable alternative. The bonding geometry of 2-methyl-2-propanethiol is not known.

It is not likely that the coverage-dependent kinetics are due to repulsive steric interactions between the methyl groups of the 2-methyl-2-propyl thiolate intermediate and the Mo(110) surface. Previously, interaction between the methyl groups of 2-propanol and the Fe(100) surface have been proposed to destabilize the 2-propoxide intermediate.[38] A similar effect could lead to destabilization of the 2-methyl-2-propyl thiolate intermediate and to desulfurization at lower temperatures. Electron energy loss spectra also argue against this explanation, as the 2-methyl-2-propyl skeleton is relatively unperturbed in the vibrational spectrum, since the loss energies agree well with gas-phase values. Rather, the kinetics of 2-methyl-2-propyl thiolate desulfurization become more complex with increasing thiolate coverage. At low 2-methyl-2-propyl thiolate coverages (Figure 4), desulfurization leads to isobutane and isobutene with relatively simple kinetics. However, as the coverage increases, the kinetics become more complex. This is most readily explained on the basis of a varying amount of sulfur deposition during the course of reaction.

Conclusions

2-Methyl-2-propanethiol on Mo(110) reacts via three competing channels on Mo(110): thiolate hydrogenolysis yielding isobutane, C–S and C–H bond scission to produce isobutene and nonselective decomposition producing adsorbed carbon and sulfur and gaseous dihydrogen. X-ray photoelectron and high resolution electron energy loss spectra establish that 2-methyl-2-propyl thiolate is formed upon adsorption. At saturation coverage, ~80% of the 2-methyl-2-propanethiol produces hydrocarbons, while ~20% reacts nonselectively. The rate and selectivity for hydrocarbon production depend on the coverage of sulfur, hydrogen, surface thiolate, and, possibly, hydrocarbon fragments in a complex fashion. The initial rate of hydrogenolysis of 2-methyl-2-propyl thiolate is faster than primary thiolates, such as the ethyl derivative, suggesting that hydrogenolysis kinetics correlate with the homolytic C–S bond strength.

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Registry No. Mo, 7439-98-7; 2-methyl-2-propanethiol, 75-66-1; isobutane, 75-28-5.

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Inclusional Complexes of Decyltrimethylammonium Bromide and β-Cyclodextrin in Water

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The inclusional process of decyltrimethylammonium bromide (DTAB) into the cavity of β-cyclodextrin (β-CD) has been studied by measuring speed of sound (u) of aqueous solutions of DTAB in the presence of various constant concentrations of β-cyclodextrin at 298.15 K. The predominant complex formed has a stoichiometry of 1:1. The apparent critical micellar concentration, cmc* (the cmc for the system DTAB + β-CD + H_2O), is found to increase upon the addition of cyclodextrin, while the concentration of free surfactant available for the micellization process in the presence of β-CD ($[DTAB]_f$) increases slightly. The binding or association constant of the complexation equilibrium is evaluated from u measurements by using a nonlinear regression method. The resulting K value is analyzed and compared with those given by other researchers and the discrepancies are discussed.

Introduction

Cyclodextrins (abbreviated as CD's hereafter), which are cyclic α(1 → 4) linked oligosacharides built up from six (α-CD), seven (β-CD), and eight (γ-CD) α-D-glucopyranose units, form inclusion compounds with smaller molecules which fit into their 5–8-Å cavity. The most important feature of these compounds is that the "host" component can admit "guest" molecules without any covalent bonds being formed.[1–3]

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