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The Role of Disulfide Linkages in Desulfurization Chemistry: The Reactions of Benzenethiol on a Sulfur-Covered Mo(110) Surface

M. K. Weldon,[‡] M. E. Napier,[‡] Benjamin C. Wiegand,[†,‡] C. M. Friend,[*,‡] and P. Uvdal[§]

Contribution from the Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138, and MAX-Chemistry, Department of Chemistry, Lund University, S-221 00 Lund, Sweden

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Abstract: The reactions of benzenethiol on a sulfur-covered Mo(110) surface were studied using temperature programmed reaction, X-ray photoelectron, and high resolution electron energy loss spectroscopies. The sulfur overlayer profoundly alters the kinetics and selectivity for desulfurization and dehydrogenation. By using isotopic labeling, we have established that phenyl disulfide (C_6H_5S–S–) is formed via S–H bond scission and S–S bond formation on Mo(110) at 100 K. The S–S– linkage is oriented perpendicular and the phenyl ring parallel to the surface. The disulfide subsequently forms an upright phenyl thiolate species, bound directly to the Mo(110) surface, prior to the onset of benzene formation at 300 K. In contrast to the clean surface, where only the low-temperature state is observed, a second benzene peak is observed at 500 K on the sulfur-covered surface. This feature is attributed to disproportionation of surface phenyl groups to produce gaseous benzene and surface benzyne. In addition, gaseous phenyl also desorbs from the surface in the same temperature range, due to a lack of available surface hydrogen. The selectivity for gaseous hydrocarbon production is approximately 80%, nearly twice that on the clean surface, while the total amount of reaction remains the same. These effects are attributed to (i) the initial phenyl disulfide formation, which anchors the reactant to the crowded surface, while preventing low-temperature decomposition, and (ii) stabilization of higher temperature intermediates, such as phenyl thiolate, surface phenyl, and benzyne (all of which possess a predominantly perpendicular ring orientation), by site-blocking by the sulfur overlayer.

Introduction

Industrial catalysts employed in hydrodesulfurization reactions usually consist of a MoS_2 moiety on a variety of substrates.[1] In an attempt to model these reactions, studies of the related desulfurization processes have been performed under ultra-high-vacuum conditions on clean, single-crystal metal surfaces.[2–6] In particular, the effect of sulfur on reactivity and the identity of surface intermediates is of interest.[4]

While there have been several investigations of thiols on clean metal surfaces, to our knowledge, no ultra-high-vacuum studies have addressed the effect of sulfur on the desulfurization of thiols, even though it is known to profoundly alter reaction kinetics[4,5] and is an integral part of the industrial catalyst. Consequently, we have undertaken the study of benzenethiol on a sulfur-covered molybdenum surface by thermal, vibrational, and core-level spectroscopies, in order to better model the desulfurization process.

The reactions of benzenethiol on clean Mo(110) have been previously studied[6] and are well understood, making this a good system for investigation on a sulfur-covered surface. Furthermore, the selectivity for hydrogenolysis, the only pathway leading to hydrocarbon formation, is only ~50% on clean Mo(110), so that the clean surface results provide a good comparison for enhanced selectivity when sulfur is present. Phenyl thiolate is formed upon adsorption at 120 K on clean Mo(110).[6] The thiolate intermediate subsequently undergoes competing C–S bond hydrogenolysis to form gaseous benzene, or C–S and C–H bond scission to form surface benzyne. The surface phenyl thiolate and benzyne intermediates were identified using high resolution electron energy loss, X-ray photoelectron, and temperature programmed reaction spectroscopies.[6] The orientation of each intermediate was determined to be nearly perpendicular to the surface plane, using near edge X-ray absorption fine structure measurements.[7,20]

Benzenethiol has also been investigated on other surfaces. A perpendicular orientation has previously been suggested for benzenethiol on Cu(111), where it was proposed to bond to the surface through a lone electron pair on sulfur, with the benzene ring oriented nearly perpendicular to the surface.[8] Unfortunately, the reactivity of benzenethiol on the Cu(111) surface was not reported. Benzene is formed from benzenethiol desulfurization on Ni(110) and a tilted geometry was proposed in this case, although no detailed analysis was performed.[9] The ability to make orientational or other detailed arguments based on vibrational spectra relies upon accurate assignment of the losses. This is difficult for complex molecules such as benzenethiol, where the large number of vibrational modes result in overlapping peaks in electron energy loss spectra. By using isotopic labeling, we have been able to unambiguously assign the vibrational losses of the dominant surface intermediates for the first time, and thus correlate the observed reactivity with adsorbate identity and geometry. Specifically, we have identified a phenyl disulfide intermediate on the surface at the 100 K. The S–S bond of the disulfide subsequently cleaves, forming adsorbed phenyl thiolate which, in turn, reacts to form benzene and adsorbed phenyl. The phenyl, in turn, produces gaseous phenyl and benzene as well as an adsorbed hydrocarbon—proposed to be benzyne. Models of the surface and disulfide show that interaction of the phenyl ring with the substrate is hindered by the sulfur overlayer. This is consistent with the nearly perpendicular geometry observed for the phenyl thiolate on the sulfur-covered surface. We relate these observations to the decrease in nonselective decomposition on the sulfur-covered surface relative to the clean surface.

[‡] Harvard University.

[†] Current address: Procter and Gamble, Cincinnati, OH.

[§] Lund University.

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Experimental Section

All experiments were performed in three different ultra-high-vacuum chambers described previously—all having base pressures of $\leq 2 \times 10^{-10}$ Torr.[5,10,11] The Mo(110) surface was cleaned before each experiment by oxidation at 1200 K in 1×10^{-9} Torr of O_2 for 5 min. The crystal temperature was allowed to return to ~200 K before flashing to 2300 K for 30 s, to remove residual oxygen. No surface carbon, oxygen, or sulfur were detected in Auger electron spectra of the surface recorded immediately prior to benzenethiol adsorption. A sharp (1×1) low energy electron diffraction pattern was also observed. The sulfur-covered Mo(110) surface chosen for study is a well-ordered surface and has a sulfur concentration measured to be 0.35 ML. A p(2×2) LEED pattern is observed for sulfur coverages in the range of ~0.25–0.4 ML. Therefore, it was important to utilize both Auger electron and X-ray photoelectron spectroscopies to determine the surface sulfur coverage. The sulfur coverage was calibrated by recording the Auger ratio for a known sulfur coverage of 0.5 ML, as verified by the observation of a p(4×1) LEED pattern.[4,12] A given sulfur coverage was then quantified by linear extrapolation of this ratio. The exact binding site of the adsorbed sulfur is not known, but it is proposed to reside in the hourglass troughs.[13]

The sulfur-covered Mo(110) surface was prepared by dosing H_2S at $\sim 1 \times 10^{-9}$ Torr, for 2 min, with the crystal maintained at a temperature of 1400 K. After the crystal was cooled to 300 K, it was annealed again to 1400 K for 1 min. Auger electron spectroscopy was used to measure the sulfur concentration on the surface; the sulfur coverage was determined to be 0.35 ± 0.05 ML. The sulfur concentration was varied over a range of 0.3–0.5 ML with little effect on the reaction kinetics. However, at a coverage of 0.35 ML, the maximum amount of benzene was produced. Furthermore, the saturation coverage of benzenethiol decreased for initial sulfur coverages above 0.35 ML.

The deuterium coadsorption experiments were performed by exposing the sulfur-covered surface to $\sim 1 \times 10^{-8}$ Torr of D_2 for 60 s at 170 K, resulting in a saturation coverage of atomic deuterium, as determined by temperature programmed desorption of the as-treated surface.

Benzenethiol (Aldrich gold label, 99+%) was dried over sodium sulfate and distilled under an atmosphere of dry nitrogen. The purity was verified frequently by mass spectrometry during the course of experiments. The mass spectra agreed very well with those reported in the literature,[14] although small amounts of benzene (<5%) persisted in the sample, even subsequent to distillation. Benzenethiol-d_5 was synthesized according to the procedure described by Miura and Kinoshita.[15] It was purified by successive distillations under nitrogen. Mass spectrometric analysis of the sample showed that the major contaminant was benzenethiol-d_0 (~10%), together with small amounts of benzene-d_0 and benzene-d_5. Benzene (Mallinckrodt, analytical grade) was used as received. All liquids were degassed by several freeze–pump–thaw cycles before use each day. The following gases were obtained from Matheson and used without further purification: dihydrogen (99.9995%), dideuterium (99.0%), hydrogen sulfide (99.5%), and dioxygen (99.8%).

X-ray photoelectron spectroscopy data were collected using a Physical Electronics ESCA 5300 system employing a Mg anode (photon energy = 1253.6 eV). The X-ray photoelectron spectra of three elements, C(1s), S(2p), and Mo(3d), were recorded during each experiment. The acquisition time for a single experiment varied between 15 and 20 min. All dosing of the crystal was performed at 120 K. Similarly, the crystal was cooled to 120 K prior to collection of X-ray photoelectron spectroscopy data. There was no evidence of charging of the crystal during an experiment, nor was there evidence for any X-ray induced decomposition. Spectra of clean Mo(110) were also collected and used for background subtraction. All binding energies were referenced to the Mo(110) Fermi level and calibrated against the $Mo(3d_{5/2})$ peak at 227.7 eV. Because spin–orbit coupling exists in the S(2p) state, there are two peaks associated with each sulfur chemical state. The two peaks are separated by 1.2 eV and have a relative intensity of $I[S(2p_{3/2})]:I[S(2p_{1/2})] = 1.8$.

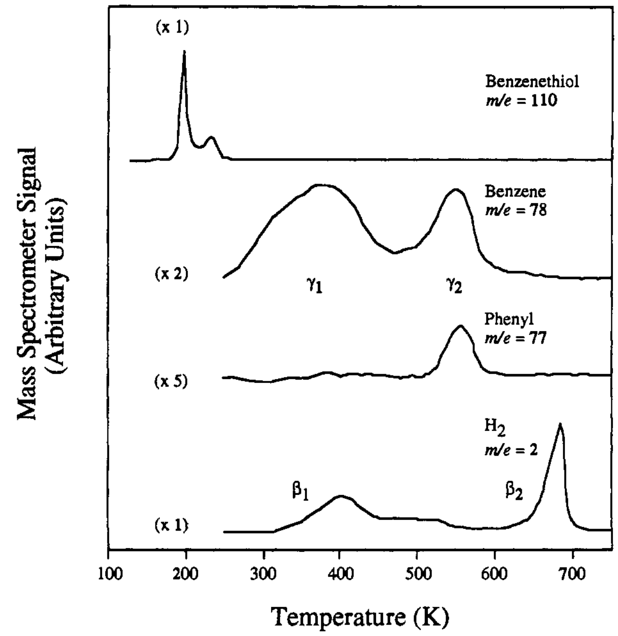

Figure 1. Temperature programmed reaction data for a multilayer exposure of benzenethiol on sulfur-covered Mo(110). A heating rate of ~15 K/s was used. All ions monitored are those of the parent molecule. The contribution from benzene cracking has been substracte from the phenyl (m/e = 77) spectrum.

The high resolution electron energy loss spectrometer (LK technologies, model LK2000) was operated at a primary energy of 3 eV, with a spectral resolution of 70–80 cm^{-1}. Temperature-dependent electron energy loss spectra were recorded by dosing benzenethiol at a crystal temperature of 100 K and then flashing the crystal to the desired temperature. The crystal temperature was allowed to return to 100 K before data collection was initiated.

The crystal was biased at −60 eV during temperature programmed reaction to minimize reactions induced by electrons emitted by the quadrupole mass spectrometer. Without the retarding voltage we found that, at high coverage, benzenethiol decomposed to diphenyl mono- and disulfide which had peak temperatures of 300 and 325 K, respectively, in the temperature programmed reaction spectrum. Importantly, no decomposition was observed with electron energies comparable to those used in electron energy loss spectroscopy, validating the use of this technique to probe the adsorbate layer. It is interesting to note that no decomposition was observed below saturation, in complete agreement with the previous work of Huntley.[9]

Results

I. Temperature Programmed Reaction Spectroscopy. Benzene is the major hydrocarbon product formed during temperature programmed reaction of benzenethiol on a sulfur-covered Mo(110) surface (Figure 1).[16] Phenyl is also evolved at ~550 K. Nonselective decomposition to form atomic carbon and sulfur and gaseous dihydrogen is a competing pathway. No other gaseous products were detected during the course of temperature programmed reaction; in particular no other gaseous hydrocarbon or sulfur-containing species were observed in a comprehensive survey of the 2–245 amu range. Carbon and sulfur remain on the suface as determined by Auger electron spectroscopy.

Benzene is evolved in two peaks at temperatures of 380 (γ_1) and 550 K (γ_2), respectively, during temperature-programmed reaction of benzenethiol on sulfur-covered Mo(110) (Figure 1). Benzene evolution from the surface is limited by the rate of benzenethiol reaction, not by benzene desorption kinetics. Benzene desorbs below 200 K when it is adsorbed on the sulfur-covered Mo(110) surface (data not shown).

Phenyl is produced concurrently with the γ_2-benzene at 550 K based on a comparison of the m/e = 77 to 78 ratios of the pure benzene with those of the γ_1- and γ_2-benzene desorption states.

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(16) In all cases, the sulfur-covered Mo(110) surface in this paper has a sulfur coverage of 0.35 ML.

The m/e = 77:m/e = 78 ratio is 0.26 ± 0.02 both for a pure sample of gaseous benzene and for the γ_1-benzene peak. In contrast, the m/e = 77:m/e = 78 ratio for γ_2-benzene is approximately 0.46 ± 0.03. Similar results were obtained for benzenethiol-d_5.[17] No products with a mass above that of benzene were detected in a careful search of all masses up to 245 amu.

A maximum of one deuterium is incorporated into the γ_1-benzene peak during temperature programmed reaction of benzenethiol in the presence of a surface presaturated with deuterium. In contrast, no deuterium incorporation into the γ_2-benzene peak was detected, in the same experiment.[18] The absence of deuterium in the γ_2-benzene is consistent with the fact that deuterium recombination occurs at a lower temperature than does γ_2-benzene formation. The source of hydrogen for γ_2-benzene production must, therefore, be dehydrogenation of a surface intermediate.

Temperature programmed reaction of a mixture of benzenethiol-d_0 and -d_5 confirms that a single C–H(D) bond is formed during γ_1-benzene production and also demonstrates that only one is formed along the path to γ_2-benzene evolution. The ratio of m/e = 78:m/e = 83 should be the same as the ratio of m/e = 79:m/e = 84 if a single C–H(D) bond is formed during benzene production.[19] The first ratio represents addition of hydrogen to nondeuterated and deuterated intermediates, respectively, and the latter, the addition of deuterium. Indeed these ratios are the same within experimental error for both the γ_1- and γ_2-benzene peaks and the ratios are nearly one for a 1:1 mixture of benzenethiol-d_5 and benzenethiol-d_0. Hence, there are no multiple exchange events. In particular, the m/e = 80 and 81 signals are accounted for by the fragmentation of m/e = 82 and 83, respectively. The additional intensity in the 82 and 77 amu signals confirm that phenyl is formed in conjunction with γ_2-benzene.

Dihydrogen is evolved in two peaks, at 410 (β_1) and 680 K (β_2), respectively. For comparison, dihydrogen evolution following saturation of the sulfur-covered Mo(110) surface with hydrogen occurs at 360 K, with no measurable kinetic isotope effect. Temperature programmed reaction of C_6D_5SH gives rise to predominantly β_1-H_2 with only a small quantity (<3% of the total reaction) of β_1-HD and D_2, indicating that the low-temperature state results primarily from recombination of the thio-hydrogens (data not shown). Furthermore, the peak temperature for β_1-D_2 formation is ~20 K higher than that for β_1-H_2, when C_6D_5SH is used—consistent with C–D bond cleavage being the rate-limiting step in the production of β_1-D_2, but recombination limiting the rate of formation of β_1-H_2.

The β_2-dihydrogen peak must be due to nonselective decomposition of a surface intermediate containing intact C–H bonds, due to the extremely high temperature of dihydrogen evolution. Furthermore, as the benzenethiol coverage is increased, the yield of β_2-dihydrogen decreases and that of γ_2-benzene increases, indicating that they are derived from a common intermediate.

At high exposures, molecular benzenethiol desorbs at 230 K. This feature increases in intensity until a second benzenethiol desorption state appears at 200 K. A further (small) increase in the benzene yield is seen over this exposure regime until saturation of the 230 K state. The 200 K peak increases indefinitely in area as a function of exposure and is therefore attributed to sublimation of benzenethiol multilayers. There is no exchange with surface deuterium for either of the benzenethiol states based on an analysis of the m/e = 110 and 111 signals. By analogy with previous studies of benzene and phenol on Mo(110),[20,21] the state at 230 K is due to desorption from a second, or weakly bound overlayer that forms as the coverage approaches a monolayer.

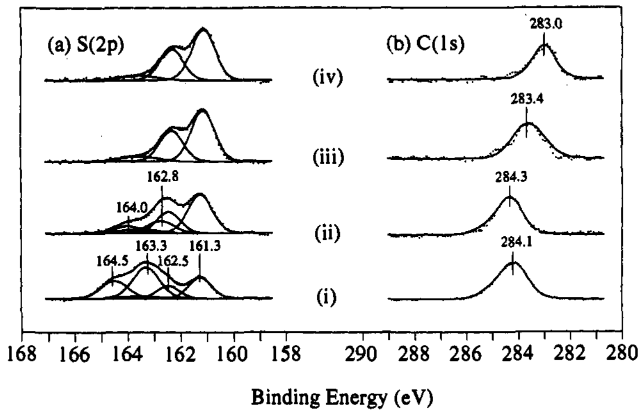

Figure 2. X-ray photoelectron spectra for (i) condensed benzenethiol and benzenethiol annealed to (ii) 275, (iii) 625, and (iv) 800 K.

A small amount of β_2-HD is also produced during temperature programmed reaction of either benzenethiol-d_0 coadsorbed with deuterium or benzenethiol-d_5. This indicates that a minor amount of reversible H–D exchange into the ring occurs, since the β_2 peaks arise from dehydrogenation of a surface intermediate, not from recombination of surface H or D. This is consistent with data obtained for C_6D_5SH, where a small amount of HD and D_2 evolution was observed at 400 K, indicating that some decomposition of the phenyl ring occurs at these temperatures.

The total amount of benzenethiol reaction on the Mo(110) surface pre-covered by 0.35 ML of sulfur is estimated to be ~0.1 ML, approximately the same as the clean surface, based an Auger data. Since no sulfur-containing products leave the surface during temperature programming, the amount of sulfur deposited after reaction of benzenethiol on the sulfur-covered Mo(110) surface is a measure of the total amount of reaction. The sulfur-molybdenum Auger ratio, $R_{S/Mo}$,[22] was determined to be 1.1 ± 0.1 for the sulfur overlayer (Θ_s = 0.35 ML) and 1.5 ± 0.1 after reaction of a saturation exposure of benzenethiol.

The selectivity for hydrocarbon formation is estimated to be ~80% based on the oxidation of carbon remaining on the surface following temperature programmed reaction. The ratio of the total CO produced from the oxidation of residual carbon on the sulfur-covered versus the clean surface was measured to be 0.36. Three sequential oxidations were required for the clean surface and six for the sulfur-covered surface. The selectivity for the sulfur-covered surface can then be estimated, given the saturation coverages for the two systems and using the selectivity of ~50%, previously determined for the clean surface using X-ray photoelectron spectroscopy.[6] Importantly, the evolution of a hydrocarbon species other than benzene is supported by a carbon-balance argument: The integrated yields of benzene and dihydrogen on the 0.35 ML sulfur-covered Mo(110) surface are less than on the clean surface, whereas the total amount of reaction is essentially the same. Therefore, reaction must occur through evolution of another hydrocarbon product, namely gaseous phenyl.

II. X-ray Photoelectron Spectroscopy. X-ray photoelectron spectroscopy demonstrates that the C–S bond of benzenethiol remains intact up to the onset of benzene formation on a sulfur-covered Mo(110) surface (Figure 2, Table 1). The peaks at 162.5

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(17) For benzenethiol-d_5, the ratio of m/e = 82 (C_6D_5) to the sum of m/e = 83 (C_6D_5H) and m/e = 84 (C_6D_6) was considered, in order to take account of the small amount of ring decomposition contributing to γ_1-benzene and exchange product in γ_2-benzene, both of which are incorporated into the m/e = 78 signal for benzenethiol-d_0.

(18) The small amount of m/e = 79 signal detected in the γ_2-benzene state is completely accounted for by the natural abundance of ^{13}C.

(19) Fragmentation of m/e = 79 with loss of H contributes to intensity in m/e = 78. The 78 amu intensity was corrected by subtracting the 79 amu fragmentation contribution. The contribution was assumed to be approximately 25% of the 79 amu signal intensity, based on the m/e = 77:m/e = 78 fragmentation ratio for d_0-benzene.

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(22) $R_{S/Mo}$ is defined as the ratio of the peak-to-peak heights measured in the derivative spectra of the following Auger signals: [Mo(LMM, 148 eV) + S(KLL, 152 eV)]/[Mo(LMM, 186 eV) + Mo(LMM, 221 eV)].

Table 1. Summary of S(2p) X-ray Photoelectron Binding Energies and Curve-Fitting Parameters

		$S(2p_{1/2})$			$S(2p_{3/2})$		C(1s)
100 K	binding energy, eV	164.5	163.3	162.5	161.3	163.5	284.1
	area, counts eV/s	1420	2420	850	1415	200	14120
	peak width, eV	1.2	1.2	1.0	1.0	1.7	1.3
275 K	binding energy, eV	164.0	162.8	162.5	161.3	163.5	284.3
	area, counts eV/s	390	665	1000	1875	325	4390
	peak width, eV	1.2	1.2	1.0	1.0	1.7	1.2
625 K	binding energy, eV			162.3	161.1	163.5	283.4
	area, counts eV/s			1450	2390	400	1130
	peak width, eV			1.0	1.0	1.7	1.5
800 K	binding energy, eV			162.3	161.1	163.5	283.0
	area, counts eV/s			1440	2380	375	1000
	peak width, eV			1.0	1.0	1.7	1.1
0.35S	binding energy, eV			162.4	161.2	163.5	
	area, counts eV/s			1080	1850	375	
	peak width, eV			0.9	0.9	1.7	

and 161.3 eV are due to the atomic sulfur in the overlayer,[23] whereas the S(2p) binding energies of 162.8 and 164.0 eV measured for benzenethiol multilayers annealed to 275 K (Figure 2a-ii) are representative of covalently bound sulfur.[24] The C(1s) peak centered at 284.3 eV is broad and asymmetric on the high binding energy side with a width of 1.2 eV following heating to 275 K—consistent with an intact C–S bond (Figure 2b-ii).

All C–S bonds are broken when condensed benzenethiol is annealed to 480 K, the temperature between the γ_1- and γ_2-benzene peaks (data not shown). There are two S(2p) peaks at 162.4 and 161.2 eV, characteristic of atomic sulfur. Importantly, the S(2p) spectra remain unchanged upon further annealing of the surface. There is a broad C(1s) peak (fwhm = 1.7 eV) centered at ~284.5 eV after annealing condensed benzenethiol to 480 K. A unique fit of this peak was not possible, but the binding energy is consistent with the carbon remaining in an environment with intact C–H and C–C bonds. Hydrocarbons typically have C(1s) binding energies in the range of 284–285 eV,[20] while atomic carbon has a binding energy of ~283 eV.[20,25]

On heating to 625 K, below the onset of β_2-H_2 formation, C(1s) X-ray photoelectron spectra show a broad peak centered at 283.4 eV (Figure 2b-iii). This is in a range similar to that previously reported for benzyne (283.4 and 283.9 eV),[6,20] although the low signal-to-noise precludes a detailed analysis. Atomic carbon is formed after annealing condensed benzenethiol to 800 K based on the single peak at 283.0 eV (Figure 2b-iv).[6,26]

The selectivity for hydrocarbon formation is confirmed to be ~80% based on the value of 0.2 obtained for the ratio of the intensity of the C(1s) peaks after heating condensed benzenethiol to 800 and 275 K, respectively. This estimate is consistent with the relative selectivity derived from the oxidation of the carbon remaining following the temperature programmed reaction. The C(1s) intensity after heating to 275 K is a measure of the total amount of benzenethiol that reacts whereas that measured after annealing to 800 K measures the amount of nonselective decomposition.

The maximum amount of benzenethiol that reacts on Mo(110) initially covered with 0.35 ML of sulfur is confirmed to be ~0.10 ML, based on the S(2p) intensities and in agreement with the Auger data. The estimate was made on the basis of the ratio of the S(2p) intensity on the freshly-prepared sulfur overlayer to that measured after reaction of benzenethiol to 800 K (Table 1).

III. High Resolution Electron Energy Loss Spectroscopy. High resolution electron energy loss spectra were obtained for condensed benzenethiol as a reference state (Figure 3a, Table 2). Losses due to the ν(S–H) and τ(S–H) modes at 2570 and 200 cm^{-1} are clearly detected for the condensed benzenethiol molecule. Assignment of the remaining vibrational losses is aided by reference to data obtained for ring-deuterated benzenethiol, C_6D_5SH (Figure 3b, Table 2).

The S–H bond is broken upon adsorption of a saturation coverage of benzenethiol on sulfur-covered Mo(110) at 100 K, as shown by electron energy loss spectroscopy (Figure 3, Table 2).[27] The vibrational data also indicate that an S–S bond is formed, producing phenyl disulfide (C_6H_5S–S–). Sulfur–hydrogen bond cleavage is clearly demonstrated by the absence of losses due to the ν(S–H) modes at 2570 and 200 cm^{-1}, respectively. With the exception of the mode at 470 cm^{-1}, all other modes are readily assigned to an intact phenyl ring by comparison to the spectra of condensed benzenethiol-d_0 and -d_5 (Figure 3, Table 2). No low energy electron diffraction pattern was observed after adsorption of a saturation exposure of benzenethiol on the 0.35 ML sulfur-covered surface, even after annealing to 700 K—a temperature at which only surface carbon and sulfur remain.

The intense mode at 470 cm^{-1}, which is not present in the spectrum of condensed benzenethiol, is assigned to an S–S stretch (Figure 3, Table 2). The assignment is made by recourse to simple geometric arguments and the organometallic literature, in combination with isotopic labeling studies. The mode at 470 cm^{-1} cannot be assigned to a surface–ring stretch, as has been previously proposed for a feature at 449 cm^{-1} for benzenethiol on Ni(110),[9] or to analogous modes for benzene π-bound to metal surfaces,[28,29] because of steric considerations. Direct interaction of the phenyl ring and the metal surface is prevented by the sulfur overlayer, even for sulfur coverages of 0.25 ML (Figure 4). Furthermore, the 470 cm^{-1} mode is not due to the C_6H_5S–Mo stretch as this mode is expected to have a frequency well below 300 cm^{-1}.[3] The 470 cm^{-1} mode could potentially correspond to a perturbed ring mode, where the perturbation could be a result of mechanical renormalization of the thiolate modes. The fact that this feature is not observed on the clean surface, at any coverage, argues against this assignment. A further possibility is that this feature is due to a ν(Mo–S$_{\text{overlayer}}$) vibration. However, the vibration associated with the sulfur overlayer on Mo(110) is located at 400 cm^{-1} and is, thus, incompatible with the intense 470 cm^{-1} loss.[4]

Isotopic labeling of the phenyl ring confirms the assignment of the 470 cm^{-1} loss as due to an S–S stretch. A downshift of ~30 cm^{-1} is predicted for a ring mode, by reference to the data for multilayers of benzenethiol-d_0 -d_5 (Figure 3a,b, Table 2). In contrast, the isotopic shift of a ν(S–S) mode on deuteration of the ring of C_6H_5S–S– is calculated to be <10 cm^{-1}, assuming simple harmonic motion, in agreement with our experimental result.

The orientation of the phenyl disulfide, shown in Figure 4, is in agreement with electron energy loss data for a saturation exposure at 100 K. Off-specular studies reveal that the out-of-plane, γ(C–H) mode at 725 cm^{-1} is almost exclusively dipole scattered, in contrast to the in-plane modes, which are predominantly impact scattered. In addition, this mode is manifold more intense than the same mode in phenyl thiolate adsorbed on the clean surface, for which the phenyl ring is nearly perpendicular to the surface, based on NEXAFS measurements.[7] Hence, these

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[23] A small peak is seen at 163.4 eV assigned as a shakeup characteristic of atomic sulfur. Its intensity was kept at 10% of the total intensity of peaks corresponding to atomic sulfur.

[24] The intensity of the atomic sulfur peaks in the spectra after annealing condensed benzenethiol to 275 K is essentially the same as for the 0.35 ML Mo(110) sulfur-covered surface (Table 1). This is consistent with all the C–S bonds remaining intact at 275 K.

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[27] Saturation is defined as the maximum coverage prior to the onset of benzenethiol desorption at 230 K. The electron energy loss spectra of even slightly higher coverages (pre-saturation of the 230 K state) reveal the appearance of features assigned to an intact sulfur–hydrogen bond, consistent with the adsorption of a weakly-bound overlayer.

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[29] Lehwald, S.; Ibach, H.; Demuth, J. E. *Surf. Sci.* **1978**, *78*, 577.

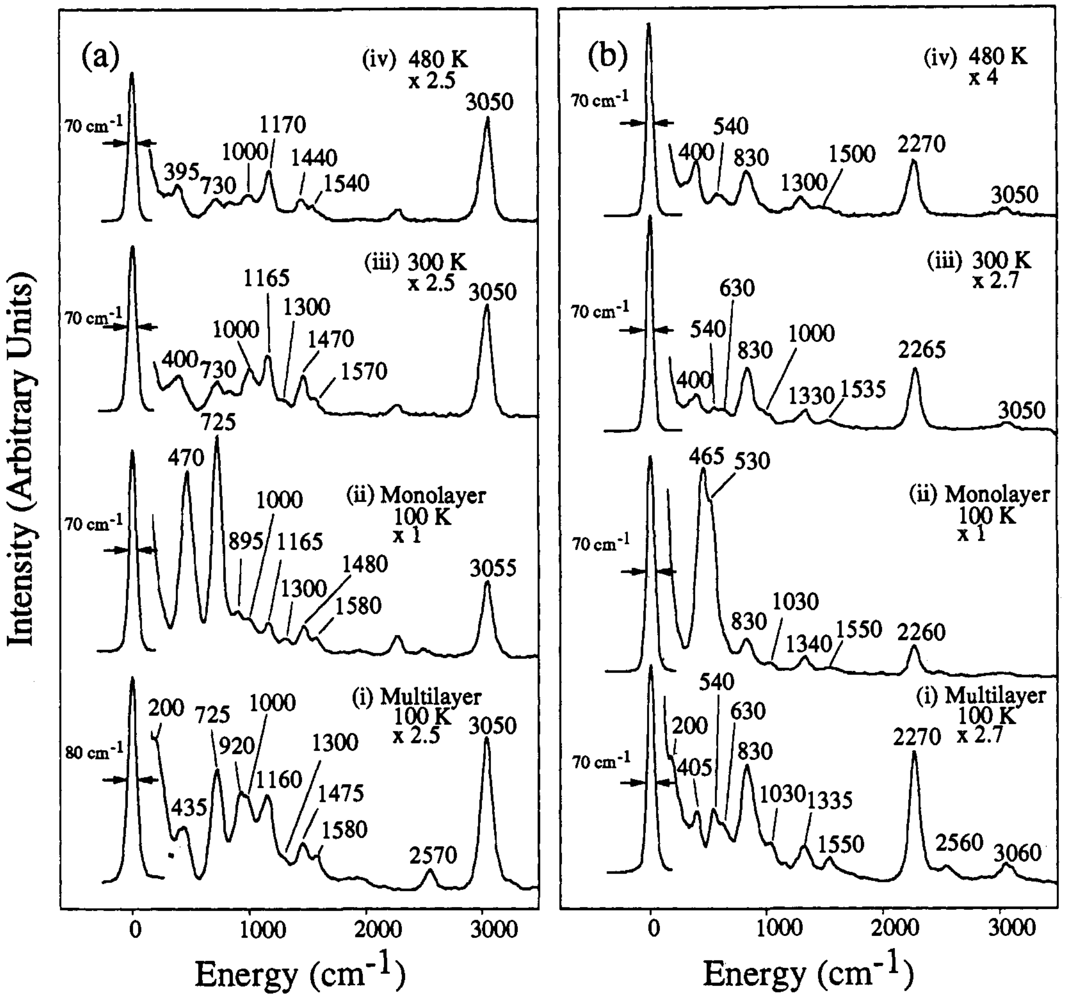

Figure 3. Electron energy loss spectra of (a) C_6H_5SH and (b) C_6D_5SH: (i) condensed multilayers at 100 K, (ii) saturation exposure at 100 K, (iii) saturation exposure, annealed to 300 K, (iv) saturation exposure, annealed to 480 K.

Table 2. Electron Energy Loss Assignments (cm^{-1}) for Benzenethiol Derivatives[a]

multilayer	monolayer		phenyl	
100 K [C_6H_5SH]	100 K [$C_6H_5S_2$–]	300 K [C_6H_5S–]	chloride [$C_6H_5Cl^{40}$]	assignments[b]
3050 (2270)	3055 (2260)	3050 (2265)	3050	$\nu(C–H)_i$
2570 (2560)	–	–	–	$\nu(S–H)$
1580 (1550)	1580 (1550)	1570 (1535)	1580	$\nu(C–C)_i$
1475 (1335)	1480 (1340)	1470 (1330)	1477	$\nu(C–C)_i$
1300 (–)	1300 (–)	1300 (–)	1322	$\nu(C–C)_i$
1160 (830)	1165 (830)	1165 (830)	1174	$\beta(C–H)_i$
– (1030)	– (1030)	– (1000)	–	$\beta(C–H)_i$
1000 (–)	1000 (–)	1000 (–)	1020	$\beta(C–H)_i$
920 (–)	895 (–)	–	902	$\gamma(C–H)_o$
725 (540)	725 (530)	730 (540)	740	$\gamma(C–H)_o$
– (630)	–	– (630)	–	$\nu(C–S)$, $\phi(C–C)_o$
–	470 (465)	–	–	$\nu(S–S)$
435 (405)	–	–	415	$\phi(C–C)_o$
–	–	400 (400)	–	$\nu(Mo–S)$
200 (200)	–	–	–	$\tau(S–H)$

[a] Numbers in parentheses were obtained using ring-deuterated benzenethiol. [b] i = in-plane, o = out-of-plane.

data are consistent with a phenyl ring orientation nearly parallel to the sulfur-covered Mo(110) surface. The coincident high intensity of the S–S stretch is in agreement with predictions based on condensed organic and inorganic disulfides, for which S–S–C bond angles in the range of 90–110° are typical.[30,31] Furthermore, the proposed orientation of the phenyl disulfide rationalizes the ~0.1 ML saturation coverage determined by X-ray photoelectron and Auger electron spectroscopy—a parallel ring orientation results in a maximum adsorbate coverage of 0.25/2 = 0.13 ML.

The phenyl disulfide is completely converted to phenyl thiolate on heating to 300 K—a temperature prior to the onset of benzene formation. The ν(S–S) mode at 470 cm^{-1} is absent and the ν(Mo–S) at 400 cm^{-1} is clearly resolved upon heating to 300 K. The out-of-plane γ(C–H) mode at 730 cm^{-1} is also severely attenuated relative to all of the in-plane modes, indicating a reorientation of the ring to a predominantly upright geometry (Table 2).[32] With the exception of the ν(Mo–S), all of the losses present at 300 K can be attributed, by reference to the electron energy loss spectrum of benzenethiol on the clean Mo(110) surface, to a phenyl thiolate species *bound directly to the surface*.[33] These observations, together with X-ray photoelectron data, suggest that phenyl thiolate is the intermediate that leads to γ_i-benzene formation.

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(30) *CRC Handbook of Chemistry and Physics*, 70th ed.; CRC Press, Inc.: Boca Raton, 1990.

(31) Weiss-Lopez, B. E.; Goodrow, M. H.; Musker, W. K.; Nash, C. P. *J. Am. hem. Soc.* **1986**, *108*, 1271.

(32) Off-specular measurements indicate that the dipole component of the scattering by the out-of-plane modes is drastically reduced on annealing to 300 K. Conversely, the in-plane modes increase dipolar intensity over the same temperature regime. This is consistent with a reorientation of the ring to a more upright geometry. Indeed, the tilt of the ring is estimated to be less than 23° away from the surface normal, because the $\gamma(C–H)_o$:$\beta(C–H)_i$ ratio for the sulfur-covered surface at 300 K is a factor of four smaller than for phenyl thiolate on the clean Mo(110) surface, for which the orientation was determined to be 23° away from the surface normal by near edge X-ray absorption fine structure experiments.[7]

(33) Weldon, M. K.; Wiegand, B. C.; Friend, C. M. unpublished results.

(34) Treichel, P. M.; Nakagaki, P. C.; Schmidt, M. S.; Rublein, E. K. *J. Organomet. Chem.* **1986**, *311*, 193.

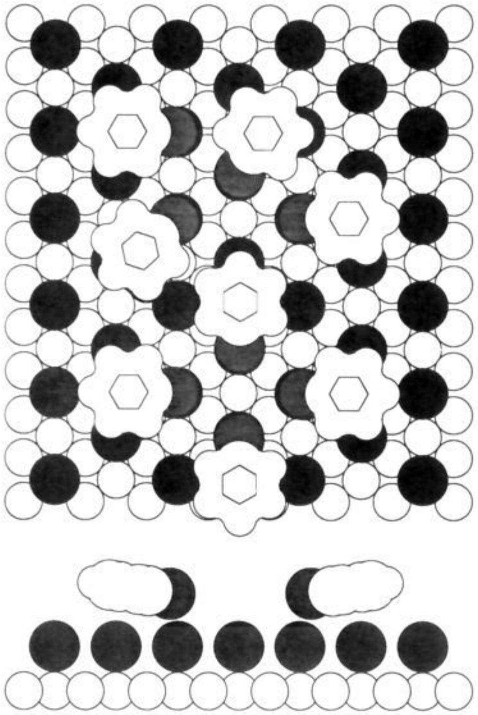

Figure 4. Schematic depiction of the Mo(110)–p(2×2)–S surface in relation to a C_6H_5S– species. The S^{2-} ionic radius was used (which is almost identical to the covalent radius of S_2) for both the thiolate and overlayer sulfur. The carbon skeleton of the phenyl ring is shown along with the associated van der Waals surface.

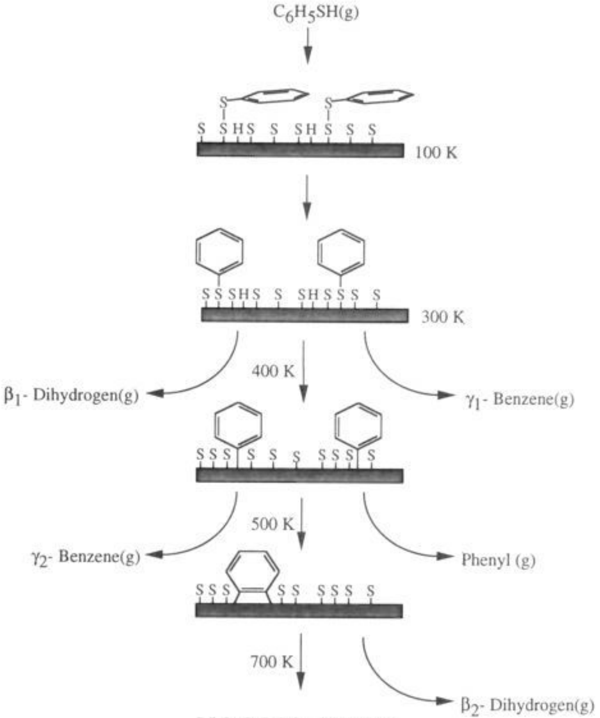

Figure 5. Proposed reaction scheme for benzenethiol on Mo(110) covered with 0.35 ML of sulfur. For the sake of clarity, stoichiometric factors have been omitted.

Other than a downshift of ~40–50 cm^{-1} in the ring modes, the vibrational spectra remain unchanged upon annealing condensed benzenethiol to 480 K, strongly suggesting that the phenyl ring is intact, albeit perturbed. Since X-ray photoelectron data obtained under similar conditions indicate that all carbon–sulfur bonds are broken, the intermediate that gives rise to the γ_2-benzene peak in the temperature programmed reaction spectrum must be an aromatic hydrocarbon. Identification of this intermediate is aided by reference to previous studies of organics on Mo(110),[20,38] for which no extensive rehydrogenation of a hydrocarbon fragment has ever been observed. In particular, rehydrogenation of benzyne on Mo(110) does *not* occur.[20] Given the appreciable concentration of this intermediate, the absence of the features characteristic of surface benzyne, at 1130 and 1425 cm^{-1},[6] is also significant. Further, based on steric considerations, the sulfur overlayer is likely to hinder the multiple coordination of hydrocarbon fragments resulting from more extensive dehydrogenation (Figure 4). Therefore, we propose that adsorbed phenyl is the most probable intermediate.

There is a general attenuation of all losses except the sulfur–metal stretch (400 cm^{-1}) upon annealing to 700 K (data not shown). Due to the high selectivity for benzene formation (80%), the concentration of remaining intermediates is very low (~0.01 ML), making a definitive characterization at temperatures above 600 K impossible. The vibrational data clearly indicate, however, that the adsorbed species retains aromatic character and has a mostly upright geometry. On the basis of this and the striking similarity of the hydrogen desorption profiles from the temperature programmed reaction spectra of benzenethiol on the clean and the sulfur-covered surfaces, we propose that the remaining intermediate is surface benzyne.

Discussion

The sulfur overlayer on Mo(110) modifies the selectivity and kinetics for benzenethiol reaction. The selectivity for hydrocarbon production is substantially higher on the sulfur-covered surface than on clean Mo(110): ~80% compared to ~50% at reaction saturation. Furthermore, the kinetics for benzene evolution are substantially different on the sulfur-covered surface. The peak temperature for γ_1-benzene evolution is ~40 K higher on the sulfur-covered surface ($\theta_s = 0.35$). Indeed, at low coverage, C–S bond scission occurs below 225 K on clean Mo(110), although no benzene is produced. The kinetics for ring dehydrogenation are also markedly slower on the sulfur-covered surface; the peak temperature for the β_2-dihydrogen is ~50 K higher than on clean Mo(110). γ_2-Benzene, which requires some ring dehydrogenation, is also exclusively produced during temperature programmed reaction on the sulfur-covered surface.

The proposed reaction scheme shown in Figure 5 is consistent with all of our observations and is proposed for sulfur coverages above ~0.2 ML. Electron energy loss data clearly indicate that phenyl disulfide and adsorbed hydrogen are formed from benzenethiol on sulfur-covered Mo(110) at 100 K. Organic disulfides are known to coordinate to molybdenum centers in organometallic complexes.[34] Indeed, disulfide formation is predicted to be slightly exothermic ($\Delta H_f \approx -15 \pm 10$ kcal/mol) for all thiols, based on bond strength arguments alone. However, thiolate formation is significantly more exothermic, so that at low sulfur coverages, the thermodynamically favored thiolate forms directly. In contrast, at high initial sulfur coverages (above 0.2 ML), low-temperature thiolate formation is not possible and

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(35) Treichel, P. M.; Nakagaki, P. C. *Organometallics* **1986**, *5*, 711.

(36) Wiegand, B. C.; Uvdal, P.; Friend, C. M. *Surf. Sci.* **1992**, *279*, 105.

(37) The carbon–sulfur stretching frequency is expected in the 600–700 cm^{-1} region, by analogy with other thiols.[3,36,39]

(38) Weldon, M. K.; Friend, C. M. manuscript in prepartion.

(39) Albert, M. R.; Lu, J. P.; Bernasek, S. L.; Cameron, S. D.; Gland, J. L. *Surf. Sci.* **1988**, *206*, 348.

(40) Whiffen, D. H. J. *J. Chem. Soc., Perkin Trans. 2* **1956**, 1350.

the disulfide formation predominates. Furthermore, formation of such disulfide linkages is expected to be quite general for thiols adsorbed on sulfur-covered Mo(110). Studies of other thiols are planned to test for the generality of disulfide formation. The disulfide formation has several effects on the reactivity of benzenethiol. Firstly, formation of the S–S bond allows the thiol to adsorb even though the Mo atoms are not accessible at 100 K (Figure 4). Indeed, it is this disulfide linkage that enables a saturation coverage of benzenethiol similar to that known for the clean surface to be attained. Furthermore, the overlayer significantly reduces interaction of the phenyl ring with the surface, because the intervening S–S bond necessarily increases the surface–ring separation compared to phenyl thiolate, despite the fact that the ring is nearly parallel to the surface. The ring orientation is presumably dictated by the internal disulfide bonding since the bond angles are the same in condensed and adsorbed disulfides.[30,31] Thus, C–S or C–H bond scission should be less facile for the disulfide compared to the corresponding thiolate. This is generally consistent with the delay in the onset of benzene formation on the sulfur-covered surface. The delayed onset of reaction may, in itself, lead to an increase in selectivity as the greater mobility of surface hydrogen at higher surface temperatures will probably favor hydrogenation to benzene over nonselective decomposition.

The disulfide persists up to ~300 K, whereupon it is completely converted to phenyl thiolate. This is almost certainly accompanied by a partial reconstruction of the sulfur overlayer in order to accommodate the thiolate, as up to 0.7 ML of sulfur can be adsorbed on Mo(110).[12] Furthermore, such low-temperature mobility of sulfur overlayers has previously been reported by Bauer et al.[12] Disulfide linkages of the form $C_6H_5SSC_6H_5$ have been used to synthesize thiolates in organometallic complexes such as $Mo(SPh)(CO)_3(\eta\text{-}C_5H_5)$.[35] The conversion to the thiolate is accompanied by a reorientation of the ring such that it is nearly aligned with the surface normal, based on changes in the intensities of the out-of-plane and in-plane C–H bending modes and comparison to the spectrum of phenyl thiolate adsorbed on clean Mo(110) for which the phenyl ring is aligned almost normal to the surface.[32] The decrease in ring tilt could result from electronic and/or steric effects. Steric reduction of the tilt angle of the phenyl thiolate would reduce coupling to the surface and hence dehydrogenation—induced via direct metal–H–C interaction. The sulfur may also perturb the bonding within the phenyl thiolate intermediate by reducing the electron density at sites neighboring the thiolate. In turn, the degree of C–S bond weakening would be decreased. Previously, vibrational spectroscopy was used to probe adsorption-induced changes in the C–S bond by analysis of the carbon–sulfur stretching frequency.[36] Unfortunately, we were not able to unambiguously assign the carbon–sulfur stretching mode using electron energy loss spectroscopy due to the low resolution of the technique and the presence of other modes in the same frequency regime.[37] However, we would point out that weakening of the C–S bond *alone* is unlikely to cause radical changes in the relative amounts of selective and nonselective decomposition, as C–S bond weakening is almost certainly important to both reaction pathways.

Phenyl thiolate hydrogenolysis leads directly to γ_1-benzene formation based on the spectroscopic and isotopic labeling experiments. As surface hydrogen is depleted, the hydrogen addition step is retarded, thus favoring the formation of surface phenyl over benzene. The sulfur apparently inhibits nonselective C–H bond scission so that the phenyl remains on the surface up to ~475 K, the onset of γ_2-benzene formation. We propose that a limited amount of reversible C–H bond cleavage also occurs in this temperature regime in order to account for the β_2-HD.

We propose that adsorbed phenyl is the intermediate that leads to γ_2-benzene production. Some phenyl, in fact, desorbs from the surface in the same temperature range due to lack of surface hydrogen (Figure 1). X-ray photoelectron data indicate that all C–S bonds are broken by 480 K—excluding phenyl thiolate as the intermediate. The similarity between the vibrational data at 300 and 480 K clearly indicates the retention of aromaticity within the ring. The relatively small amount of deuterium evolution below 480 K, upon reaction of C_6D_5SH, is also consistent with the predominance of a phenyl intermediate. Furthermore, the isotopic exchange experiments show that there is a single hydrogenation step leading to benzene formation, as expected for hydrogenation of phenyl. The observation of phenyl desorption is also compelling evidence for a surface phenyl intermediate. Finally, given that surface hydrogen is obviously mobile at these temperatures, the almost complete absence of dihydrogen formation coincident with γ_2-benzene evolution implies that the mechanism involves the disproportionation of two surface phenyls, leading to γ_2-benzene and a surface benzyne intermediate. This is consistent with temperature programmed reaction data obtained for low exposures, where the γ_2-benzene state is suppressed relative to γ_1-benzene. Benzyne is proposed to be the intermediate that leads to nonselective decomposition based largely on analogy with the clean Mo(110) surface. Although all data are consistent with the presence of benzyne, the low concentration precludes unambiguous identification of this intermediate.

Conclusion

In summary, the increase in selectivity, for the same total amount of reaction of benzenethiol on the sulfur-covered surface and the clean Mo(110) surface, is attributed to two effects: (i) the initial phenyl disulfide formation, which anchors the reactant to the surface and prevents low-temperature decomposition even though the phenyl ring is parallel to the surface plane, and (ii) stabilization of higher-temperature intermediates, such as phenyl thiolate, surface phenyl, and benzyne (all of which possess a predominantly perpendicular ring orientation), by site-blocking by the sulfur overlayer. The possibility that electronic effects may also be important must be addressed by theoretical studies. Similar studies of other thiolates on sulfur-covered Mo(110) are currently under way to investigate the generality of disulfide formation and the effect on reactivity.

Finally, our work illustrates the importance of isotopic labeling in definitively identifying surface intermediates. Specifically, assignment of the ν(S–S) in the vibrational spectrum at 100 K and identification of a surface phenyl moiety at 500 K were only possible by reference to parallel studies using benzenethiol-d_5.

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