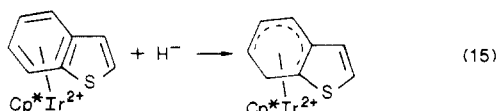
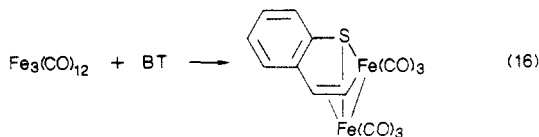


$\text{BEt}_3\text{H}^-$ ) occur by addition of  $\text{H}^-$  to the coordinated-benzene carbon atoms. The predominant product is that in which  $\text{H}^-$  adds to the 7-position (eq 15); however,



isomers resulting from  $\text{H}^-$  addition to the 4-, 5-, and 6-benzene ring positions are also observed. As expected, the metal in these complexes activates the benzene ring to react but does not lead to likely HDS intermediates<sup>71</sup> in which C-S bonds are cleaved or the 2,3-positions are hydrogenated.

An interesting reaction with  $\text{Fe}_3(\text{CO})_{12}$  that does lead to C-S bond cleavage<sup>47</sup> gives a benzothiaferrole product in which a  $\text{Fe}(\text{CO})_3$  group inserts into a C-S bond (eq 16). Although the low oxidation state of Fe in  $\text{Fe}_3(\text{C}-$



$\text{O})_{12}$  may be more reactive than might be expected of a metal site on an HDS catalyst, especially a Mo-based catalyst, reaction 16 is at present the only model reac-

tion of BT that suggests a reasonable first step in the process. In fact, under  $\text{H}_2(\text{g})$  at 175 °C, the benzothiaferrole in eq 16 gives ethylbenzene, the major product of BT HDS.<sup>71</sup>

### Concluding Comments

The model complex and catalytic reactor studies of thiophenes summarized in this Account have allowed us to formulate thiophene HDS mechanisms that are based for the first time on known chemistry. They are still proposals at this stage, but they are sufficiently detailed to allow rigorous testing. As noted, some of the tests have already been passed; others are yet to be done. Mechanisms for benzothiophene are not as well developed; however, it seems likely that the combination of organometallic chemistry and heterogeneous reactor studies will yield reasonable mechanisms for this organosulfur compound as well.

*I am grateful to the graduate students and postdocs who largely shaped our HDS studies described in this report. Also, many thanks go to Professor Glenn L. Schrader, who guided me and my students through the mysteries of HDS from the chemical engineer's viewpoint, and to the Department of Energy (Office of Basic Energy Sciences, Chemical Sciences Division), who encouraged and funded our research in this field.*

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## Deduction of Reaction Mechanisms for Surface Processes: Desulfurization of Organic Sulfides and Thiols on Mo(110)

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The investigation of desulfurization processes on single-crystal surfaces is motivated by the need to understand the related hydrodesulfurization process, whereby sulfur is removed from fuel feedstock with a sulfided molybdenum catalyst. Sulfur is removed from fuel feedstock in order to minimize production of environmentally deleterious sulfur oxides in combustion and to reduce the deactivation of automobile catalytic converters, which are poisoned by sulfur. Although

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considerable efforts have recently been made to understand model desulfurization reactions on single-crystal transition-metal surfaces,<sup>1-9</sup> there is still controversy as to the relative importance of C-S bond cleavage and C-H bond formation in controlling desulfurization rates.

Our work focuses on the reactions of a series of structurally related cyclic sulfides and linear thiols on Mo(110): the saturated  $\text{C}_2$  through  $\text{C}_5$  cyclic sulfides, linear thiols, and benzenethiol. In this paper, we demonstrate how the mechanisms of relatively complex surface reactions are deduced by using a unique marriage of the methodologies of physical organic chemistry

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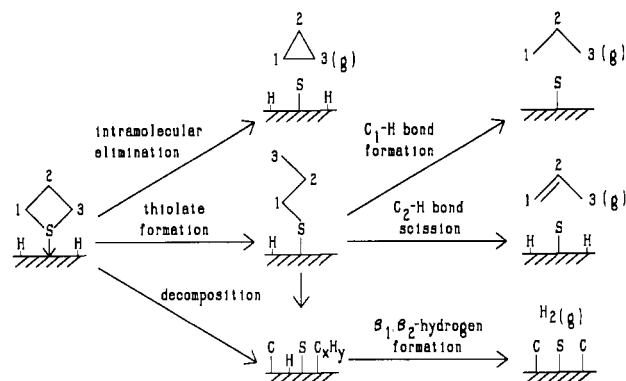
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**Figure 1.** The three competing reaction channels for trimethylene sulfide on Mo(110). No molecular desorption of trimethylene sulfide occurs from the Mo(110) surface.

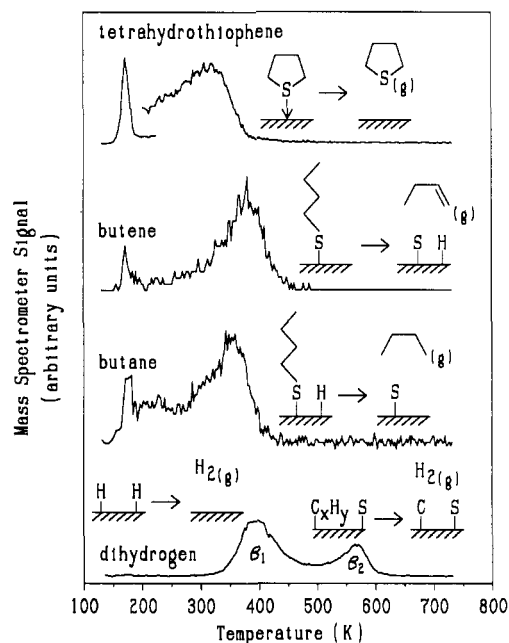
and surface spectroscopy. The comparison of these structurally related S-containing molecules clearly demonstrates that ring opening plays an important role in determining the kinetics and selectivity for Mo-catalyzed desulfurization processes. The (110) is the closest packed, lowest free energy surface of molybdenum and was chosen because of its stability, so that reconstruction or rearrangement of the molybdenum surface atoms would not occur during reaction.

The general mechanism for the reaction of cyclic sulfides on Mo(110) deduced from our work is illustrated in Figure 1 for trimethylene sulfide.<sup>2</sup> There are three competing channels for reaction of cyclic sulfides: (1) irreversible decomposition to gaseous dihydrogen and surface carbon and sulfur, (2) formation of a thiolate intermediate, which subsequently forms linear hydrocarbons, and (3) intramolecular hydrocarbon elimination. In the case of the C<sub>4</sub> and C<sub>5</sub> sulfides, reversible molecular desorption is a competing channel. Furthermore, we have shown that alkanethiols react via the thiolate channel shown in the figure. Several principles governing reactivity of these S-containing molecules have been established from our work: (1) the enthalpy of ring opening of cyclic sulfides plays a key role in determining reaction selectivity and activity; (2) the ring size is important in determining selectivity for C-C bond formation; (3) the kinetics for hydrocarbon formation from primary thiolates is independent of alkyl chain length; (4) the kinetics and selectivity for hydrocarbon formation depend strongly on the coverages of *molecular fragments*, such as a thiolate intermediate, as well as S, C, and H.

### Chemical Identification of the Thiolate Intermediate

Our primary tool for probing reaction kinetics and deducing the mechanism of surface reactions is temperature-programmed reaction spectroscopy.<sup>10</sup> The identity of surface-stable intermediates has been confirmed and their structure determined spectroscopically, but temperature-programmed reaction studies are essential for defining *kinetically* relevant processes. To illustrate the temperature-programmed reaction method, representative spectra for tetrahydrothiophene on Mo(110) are shown in Figure 2. In a temperature-programmed reaction experiment, a reactant molecule is dosed on to the surface at a base temperature,

(10) See, for example: Madix, R. J. *Science (Washington, D.C.)* 1986, 233, 1159.



**Figure 2.** Temperature-programmed reaction spectra for tetrahydrothiophene on Mo(110). Multilayers of tetrahydrothiophene, which sublime at 165 K, have been adsorbed at a surface temperature of 120 K and subsequently heated at a rate of 16 K/s. Some competing, irreversible nonselective decomposition of the tetrahydrothiophene also occurs prior to thiolate formation. Carbon and sulfur remain on the surface as nonvolatile products.

120–160 K in our experiments. The amount of reactant exposed to the surface can also be varied to determine the surface concentration dependence of the reactions. Unless otherwise noted, the results discussed here are in the limit of high surface concentration; measurements at lower coverages are described in our original publications. Following this exposure, the reactant-covered surface is heated at a linear rate, resulting in either desorption or surface reaction, and the volatile products are monitored mass spectrometrically. The temperature at which the rate of appearance of a gaseous species is at a maximum is a measure of the activation barrier for desorption or reaction, depending on which process is rate limiting, and is modeled with Arrhenius kinetics.

Tetrahydrothiophene reacts to form butane, butene, and H<sub>2</sub>, leaving carbon and sulfur on the surface (Figure 2). A small amount of tetrahydrothiophene reversibly desorbs from the surface, reaching a maximum rate at 280 K, corresponding to a desorption energy of 18 kcal/mol.<sup>11</sup> Approximately 25% of the tetrahydrothiophene that reacts forms hydrocarbons while 75% irreversibly decomposes to form carbon, sulfur, and dihydrogen. Irreversible decomposition occurs via more than one path, both prior to and after thiolate formation. The hydrocarbon production channel leads to the formation of butane and butene with the peak temperatures of 350 and 370 K, respectively, indicating that the rate of butane formation is faster than butene formation.<sup>12</sup> Furthermore, the rate of butane pro-

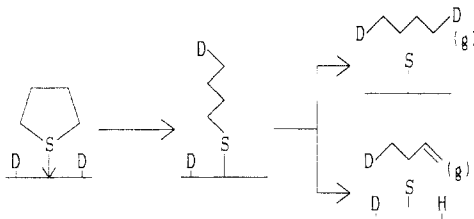
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(12) The fact that desorption of butane and butene is not rate limiting is established by measuring the desorption temperature (energy) for butane and butenes on clean and sulfided Mo(110). Butane and all isomers of butene desorb from Mo(110) below 250 K, lower than the temperature where they are produced from the reaction of tetrahydrothiophene.

duction falls dramatically while the butene production rate increases when gaseous  $H_2$  formation commences. These observations suggest that butane and butene are formed via competing hydrogenation and dehydrogenation of a common intermediate. The logical intermediate is the butanethiolate.

We obtained support of this mechanism by measuring the change in the relative rates of butane and butene production when tetrahydrothiophene is reacted in the presence of adsorbed H or D. Since hydrogenation of the thiolate is proposed to be the rate-limiting step in butane formation, the rate of butane production is predicted to increase with increasing surface coverage of H or D during reaction. In fact, the rate of butane formation does increase when tetrahydrothiophene reacts in the presence of hydrogen atoms on the surface, as expected if C-H bond formation is kinetically important.

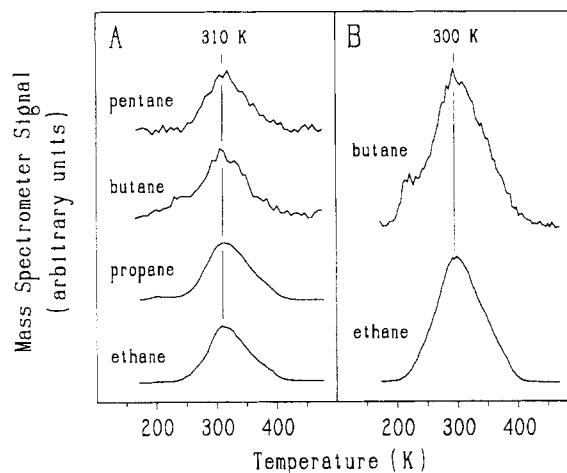
The isotopic distribution of the hydrocarbon products formed when tetrahydrothiophene is reacted in the presence of adsorbed deuterium atoms further supports our mechanism. As predicted by this mechanism, two C-H(D) bonds are formed to produce butane while one C-H(D) is formed to yield butene:



We propose selective hydrogenation of the carbon adjacent ( $\alpha$ ) to the sulfur in the thiolate to form butane or selective dehydrogenation at the 2-carbon ( $C_\beta$ ) of the thiolate in formation of 1-butene.

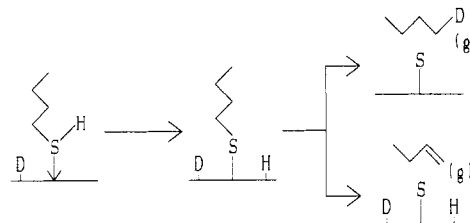
In order to further test the mechanism, we studied the reactivity of the butanethiolate intermediate by preparing it from reaction of 1-butanethiol on Mo(110). Spectroscopic evidence demonstrates that the thiolate intermediate is formed from thiols at 120 K: the  $\nu(S-H)$  mode is absent in vibrational spectra and a chemical shift in the S(2p) binding energies is observed (see below).<sup>18-20</sup> If 1-butanethiol and tetrahydrothiophene both react via the thiolate with the same rate-limiting step, the product distributions and reactions rates for the two molecules will be same with the caveat that differences in the concentrations of other species on the surface, such as atomic hydrogen or sulfur, may affect the reaction kinetics.

Indeed, butane and butene are formed in the temperature-programmed reaction of 1-butanethiol on Mo(110) with kinetics similar to their production from tetrahydrothiophene and adsorbed hydrogen atoms, lending strong evidence for reaction of tetrahydrothiophene and 1-butanethiol via a common, butanethiolate intermediate. Further, as predicted by our



**Figure 3.** Alkane production from the temperature-programmed reaction of mixtures of linear thiols and cyclic sulfides on Mo(110): (A) ethanethiol, 1-propanethiol, 1-butanethiol, and 1-pentanethiol; (B) ethanethiol and tetrahydrothiophene. The correspondence in the peak temperatures and line shapes for alkane production shows that the kinetics for alkane elimination are the same for the sets of molecules reacted in the two experiments.

mechanism, reaction of 1-butanethiol with deuterium atoms on the surface yields only butene- $d_0$ , butane- $d_0$ , and - $d_1$ :



Moreover, investigation of the reactions of the  $C_2$ - $C_5$  primary alkanethiols on Mo(110) has established that thiolate formation followed by linear hydrocarbon production is a general mechanism for this class of reactants.<sup>3</sup> Temperature-programmed reaction of  $C_2$ - $C_5$  linear alkanethiols all resulted in selective formation of their respective alkanes and alkenes. In all cases, reaction of the thiol in the presence of adsorbed D results in no deuterium incorporation into the alkene and incorporation of a maximum of one deuterium atom into the alkane, as predicted by the mechanism.

Importantly, the kinetics for alkane formation from the alkanethiolates on Mo(110) are independent of alkyl chain length but dependent on coverage.<sup>3</sup> Adsorption and subsequent temperature-programmed reaction of mixtures of different alkanethiols ensure that they react on a surface with the same concentrations of H-, S-, and C-containing intermediates. The line shapes and peak temperatures for all of the alkanes formed in the temperature-programmed reaction of a mixture of ethanethiol, 1-propanethiol, 1-butanethiol, and 1-pentanethiol are virtually identical, demonstrating that the kinetics for alkane formation are independent of the alkyl chain length (Figure 3A).<sup>3</sup> Spectroscopic studies, discussed below, demonstrate that the kinetics for C-S bond cleavage are dependent on the coverage of the thiolate and that the presence of atomic sulfur is not necessary for selective decomposition. Although S does modify the kinetics and selectivity for surface reaction of the thiolates, it is *not* necessary for hydrocarbon production on Mo(110).

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(19) Roberts, J. T.; Friend, C. M. *J. Phys. Chem.*, in press.

(20) Roberts, J. T.; Friend, C. M. *Surf. Sci.* 1988, 198, L321.

Using the fact that the kinetics for alkane production from an alkanethiolate are independent of chain length, we confirmed that the cyclic sulfides produce linear alkanes via a thiolate intermediate. If both react via their respective thiolate intermediates, temperature-programmed reaction of a mixture of tetrahydrothiophene and ethanethiol should result in production of butane and ethane with similar kinetics. As predicted, butane and ethane were produced with nearly identical kinetics in the temperature-programmed reaction of the mixture (Figure 3B).<sup>3</sup> Analogous experiments performed for a mixture of trimethylene sulfide and ethanethiol showed that propane is formed with kinetics essentially identical with that of ethane formation from the ethanethiolate, thus confirming that the propanethiolate is the intermediate yielding linear hydrocarbons from the desulfurization of trimethylene sulfide (Figure 1).

### Reaction Selectivity: The Roles of Ring Strain and Size

The contrasting chemistry of the C<sub>3</sub>- and C<sub>4</sub>-cyclic sulfides on Mo(110) illustrates the importance of the enthalpy of ring opening in determining selectivity. Tetrahydrothiophene undergoes competing molecular desorption, thiolate formation, and irreversible decomposition: no intramolecular elimination occurs. In contrast, competing intramolecular elimination, thiolate formation, and irreversible decomposition are observed for the C<sub>3</sub> analogue, trimethylene sulfide, with no reversible desorption (Figure 1). The intramolecular elimination of cyclopropane from trimethylene sulfide occurs at 190 K with a barrier of about 13 kcal/mol.<sup>2</sup> Reaction of trimethylene sulfide in the presence of deuterium atoms on the surface yields only cyclopropane-*d*<sub>0</sub>, showing clearly that the cyclopropane is formed in an intramolecular process.

The differences in the reaction selectivity between trimethylene sulfide and tetrahydrothiophene can be understood by considering the overall enthalpies for intramolecular elimination from the two cyclic sulfides. The ring strain energies are 2 and 19 kcal/mol for tetrahydrothiophene and trimethylene sulfide, respectively,<sup>13</sup> and the enthalpies of reaction for cycloalkane formation (intramolecular elimination) on the Mo(110) surface have been previously estimated to be -31 kcal/mol for trimethylene sulfide and -14 kcal/mol for tetrahydrothiophene.<sup>2</sup> Furthermore, the fact that molecular desorption of tetrahydrothiophene is observed while it is *not* for trimethylene sulfide is accounted for by the relative energetics for ring opening and molecular desorption in the two cases. The barrier for molecular desorption for trimethylene sulfide is expected to be similar to that for tetrahydrothiophene since both molecules should bond to the surface through the S lone pairs and have similar Lewis basicities. Therefore, the *hypothetical* desorption temperature for molecularly adsorbed trimethylene sulfide on Mo(110) is near 280 K, more than 90 K higher than the temperature required for intramolecular elimination of cyclopropane. In other words, all of the trimethylene sulfide reacts on the surface at a temperature well below that where molecular desorption can occur.

For the highly strained C<sub>2</sub> cyclic sulfide, ethylene sulfide, intramolecular elimination of ethylene with an exceedingly low activation barrier ( $\leq 6$  kcal/mol) is the

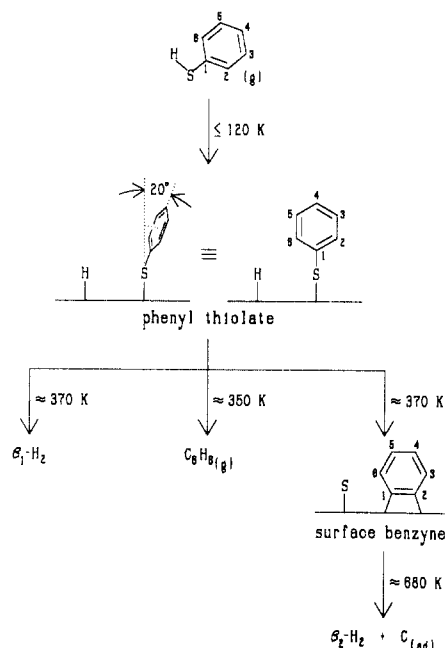
exclusive hydrocarbon production channel.<sup>14,15</sup> The preference for intramolecular elimination over thiolate formation in the case of ethylene sulfide cannot be due to an intrinsic instability of the ethanethiolate, since this thiolate is formed via reaction of ethanethiol.<sup>3,19</sup> Therefore, the intramolecular elimination of ethylene must be the *kinetically* favored channel in the reaction of ethylene sulfide. Further, ethylene sulfide eliminates ethylene very selectively: 85% of the ethylene sulfide forms ethylene compared to the hydrocarbon yields of 25% and 45% for tetrahydrothiophene and trimethylene sulfide, respectively.

This high selectivity is attributed to both a low enthalpy of activation for the intramolecular elimination of ethylene from ethylene sulfide and the small ring size. The enthalpies of reaction for intramolecular hydrocarbon elimination from ethylene sulfide and trimethylene sulfide are comparable: -34 and -31 kcal/mol, respectively. Therefore, the high selectivity for intramolecular elimination cannot be accounted for solely on the basis of the overall thermodynamics. The production of ethylene requires the formation of a C-C  $\pi$  bond. The presence of a C-C  $\sigma$  bond in the reactant ethylene sulfide is proposed to result in a low free energy of activation for C-C  $\pi$  bond formation. Since the carbon centers are already directly bonded to each other in the reactant, only a small amount of structural reorganization is required for the intramolecular elimination of ethylene. In contrast, cyclopropane elimination from trimethylene sulfide requires significant movement of the carbon centers. The two carbons in trimethylene sulfide that form a C-C  $\sigma$  bond in the intramolecular elimination reaction are separated by 2.6 Å,  $\sim 1.1$  Å greater than the C-C bond distance in the cyclopropane product.<sup>15</sup>

The kinetics for elimination of ethylene into the gas phase are suggestive of a concerted transition state. Ethylene is evolved into the gas phase from the ethylene sulfide decomposition at a surface temperature of 130 K, lower than the temperature required to desorb ethylene from the surface. This observation suggests that the transition state for ethylene formation has a large component of the momentum perpendicular to the surface, resulting in the direct formation of gaseous ethylene rather than adsorption of the ethylene product on the surface.

### Bonding and Structure of Intermediates

We have also defined the structure and temperature of formation of reactant species on the surface using spectroscopic methods as a direct complement to the chemical probes described in the preceding sections. We used two core-level electronic spectroscopies, X-ray photoelectron spectroscopy and near-edge X-ray absorption fine structure measurements, and a vibrational probe, high-resolution electron energy loss spectroscopy. Core-level binding energies, measured in an X-ray photoelectron experiment, are different for atoms in chemically distinct environments so that molecular thiols, thiolates, and atomic species can be distinguished and identified by the shift in binding energies (chemical shift). The chemical shift is used here to determine the temperature and coverage where various reactants are stable on the surface and to determine the number of chemically distinct species on the surface. In a near-edge X-ray absorption fine structure experiment, line-

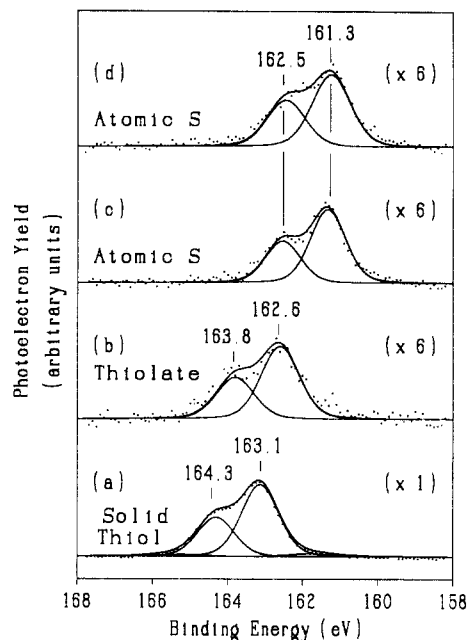


**Figure 4.** Reaction scheme for benzenethiol on Mo(110) at high coverage.

arly polarized, variable-energy photons, produced with a synchrotron source, induce electronic transitions of core electrons, e.g.,  $C(1s)$ , to unfilled molecular orbitals of either  $\pi$  or  $\sigma$  symmetry.<sup>16</sup> Molecular orientation is derived from the polarization dependence of transitions of  $\pi$  or  $\sigma$  symmetry using the dipole selection rule while bond lengths can be derived from an empirical correlation of the  $\sigma^*$  resonance energy and the internuclear separation.<sup>17</sup> High-resolution electron energy loss spectroscopy is a vibrational probe used here to aid in the identification of surface intermediates. The combination of these three methods with chemical studies is a powerful means of identifying surface intermediates and determining their structure.

X-ray photoelectron and high-resolution electron energy loss (vibrational) spectroscopies show that a surface thiolate intermediate is formed from thiols with a barrier of  $<7$  kcal/mol when adsorbed on Mo(110). The spectroscopic studies of the benzenethiolate intermediate formed from benzenethiol<sup>18</sup> will be used to exemplify our experimental approach. Analogous studies of ethanethiol<sup>19</sup> and 1-propanethiol<sup>20</sup> also indicate the presence of their respective thiolates. Benzenethiol reacts on Mo(110) by the general mechanism described above and specifically illustrated in Figure 4. The benzenethiolate, formed upon adsorption, undergoes  $C-S$  hydrogenolysis to form benzene with competing selective dehydrogenation of one of the 2-carbons forming surface benzyne.

X-ray photoelectron and vibrational spectroscopies were key in identifying the thiolate. Spectra obtained for photoejection of sulfur 2p electrons from species formed after heating of a high coverage of benzenethiol are shown in Figure 5. Two different S(2p) binding energies are associated with a single species due to spin-orbit splitting. For example, the two S(2p) binding energies measured for benzenethiol solid (multilayers) at 163.1 and 164.3 eV are characteristic of the single sulfur environment in  $(C_6H_5)SH$ . A chemical shift of  $-0.5$  eV in the S(2p) binding energies with respect to condensed benzenethiol is observed when benzenethiol

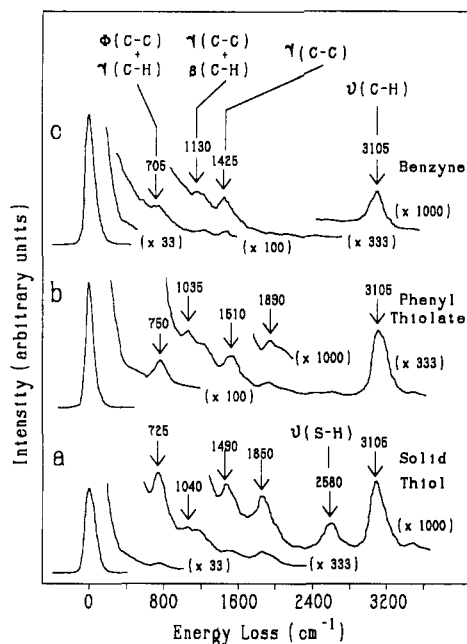


**Figure 5.** Sulfur(2p) X-ray photoelectron spectra for benzenethiol as a function of surface temperature: (a) condensed benzenethiol, a reference state; (b) benzenethiolate formed by exposure of benzenethiol to Mo(110) at 120 K; (c and d) atomic sulfur formed from heating to 600 and 900 K, respectively, above the temperature for benzene and benzyne formation.

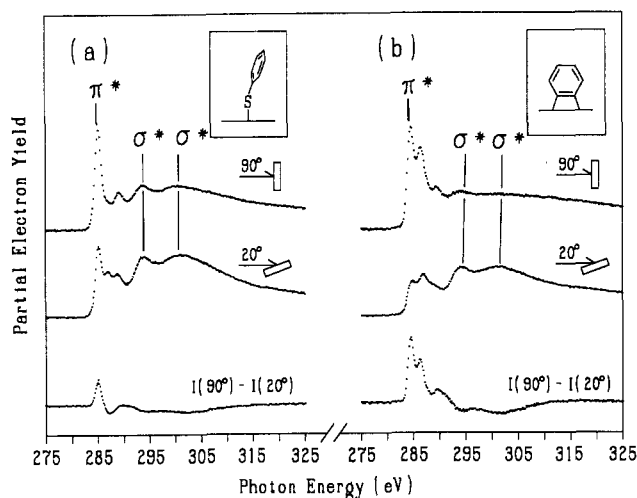
reacts on the Mo(110) surface at 120 K to form the benzenethiolate, as confirmed by vibrational spectroscopy. The X-ray photoelectron data further show that there is a *single* species present on the surface until hydrocarbon formation commences which contains covalently bound sulfur. No atomic sulfur is observed. Because there is a single covalently bound species, it must be the intermediate that reacts to form hydrocarbons, in this case benzene. Furthermore, the interpretation of complementary vibrational and structural data is simplified by the fact that a single molecular species is present. Vibrational data confirm that thiolate formation occurs upon adsorption at 120 K (Figure 6). The only significant difference in the vibrational spectra of benzenethiol solid and the species formed from its reaction at 120 K on Mo(110) is that the  $\nu(S-H)$  observed at  $2580\text{ cm}^{-1}$  in solid benzenethiol is absent in the surface species (Figure 6a,b). The ring modes are still observed and the  $\nu(C-H)$  modes are at the same frequency as for the multilayer. These observations are clear evidence for thiolate formation.

The orientation of the phenyl ring in the thiolate intermediate was determined by using the near-edge X-ray absorption fine structure method. Our work shows that the aromatic ring of the benzenethiolate has an average orientation of  $\sim 20^\circ$  with respect to the surface normal at saturation coverage (Figure 7a).<sup>21</sup> The small ring tilt is indicative of a minimal interaction of the  $\pi$  system of the ring with the metal surface and is in part attributed to intermolecular interactions at high coverage. The near-edge X-ray absorption fine structure method will prove to be a powerful method for extracting structural information for relatively complex reactants. This additional structural information will contribute to the development of structure-reactivity relationships for surface processes.

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**Figure 6.** Vibrational spectra for benzenethiol-derived intermediates formed on Mo(110): (a) condensed benzenethiol; (b) benzenethiolate at 120 K; (c) benzenethiolate formed from reaction on the surface at 550 K. Note the absence of the S-H stretch mode at  $2580\text{ cm}^{-1}$ , the constant  $\nu(\text{C-H})$  stretching frequency of  $3105\text{ cm}^{-1}$ , and the presence of ring modes ( $\phi(\text{C-C})$  and  $\gamma(\text{C-C})$ ) in the spectrum of the benzenethiolate.



**Figure 7.** C K edge near-edge X-ray absorption fine structure spectra: (a) the benzenethiolate intermediate; (b) benzyne formed from the reaction of benzenethiol on Mo(110). The polarization dependence of the  $\pi^*$  and  $\sigma^*$  peaks of the aromatic ring yield the orientation of the ring with respect to the surface.

Spectroscopic investigations are extremely important in studying surface processes where no volatile product is formed. For example, surface benzyne is formed in the competing dehydrogenation of the benzenethiolate on Mo(110) (Figure 4).<sup>18</sup> Benzyne was identified by a combination of temperature-programmed reaction spectroscopy, C(1s) and S(2p) X-ray photoelectron spectroscopy, and vibrational spectroscopy. Benzyne formation via C-S bond cleavage and selective dehydrogenation of one of the carbons ortho to the thiolate sulfur is predicted by our general mechanism, discussed above. Spectroscopic studies show that benzyne formation occurs at temperatures slightly above the maximum rate of gaseous benzene formation and is accompanied by the deposition of atomic sulfur on the

surface. The S(2p) X-ray photoelectron data demonstrate that atomic sulfur is exclusively present on the surface at 600 K (Figure 5c). Vibrational data (Figure 6c) show that the ring is intact and aromatic in character, and the ring is shown to be nearly perpendicular to the surface plane using near-edge X-ray absorption fine structure measurements (Figure 7b).

It is noteworthy that the kinetics for C-S bond cleavage are strongly dependent on thiolate coverage.<sup>18,19</sup> Although no volatile products are formed in the low-coverage limit for any of the thiols on Mo(110), thiolate formation still occurs upon adsorption. In the case of the benzenethiolate, C-S bond breaking is complete below 300 K at the lowest coverage studied. Dehydrogenation also occurs at low coverage at temperatures below those necessary for hydrocarbon formation, accounting for the predominance of irreversible, nonselective decomposition. The barriers for C-S and C-H bond scission increase with increasing coverage so that at high coverage the thiolate is stable up to temperatures where hydrogenation can occur, resulting in hydrogenolysis products. Significantly, atomic sulfur is *not* present when benzene is produced from thiolate hydrogenolysis at high coverage. Rather, the benzenethiolates self-modify their reaction kinetics. The coverage-dependent reaction kinetics could be the result of electronic, structural, or site-blocking effects, and electronic structure calculations are planned to evaluate the role of electronic effects.

X-ray photoelectron studies (data not shown) of ethylene sulfide also showed that the kinetics for ethylene elimination are strongly dependent on sulfur coverage and support the conclusion from temperature-programmed reaction experiments that intramolecular ethylene elimination and desorption occur with high selectivity at 130 K on clean Mo(110).<sup>15</sup> Our work shows that the barrier for ethylene elimination abruptly increases when  $\sim 0.25$  monolayer of sulfur is deposited on the surface. In this case, atomic sulfur modifies the desulfurization kinetics. Clearly, the application of spectroscopies is crucial to understanding the details of surface processes and is particularly powerful when complemented by chemical studies.

## Conclusions

Using a combination of physical organic and spectroscopic methods, we have demonstrated that three reaction channels compete with reversible molecular desorption in the desulfurization of cyclic sulfides on Mo(110): intramolecular elimination, thiolate formation leading to linear hydrocarbons, and irreversible decomposition. The relative importance of the four competing channels is controlled by the ring strain and size, as demonstrated by studying a series of structurally related sulfides. Primary alkanethiols form hydrocarbons, with kinetics independent of the alkyl chain length, via a thiolate intermediate with some competing irreversible decomposition. The coverage of other surface species, in particular the thiolates themselves as well as C, S, and H, effects the kinetics of hydrocarbon formation for both the cyclic sulfides and alkanethiols. Surface-stable thiolates are formed from alkanethiols on the Mo(110) surface.

While Mo-induced desulfurization reactions were the focus of this paper, our approach to understanding mechanisms of surface reactions on a molecular level

is general. Chemical probes establish trends in reactivity and suggest kinetically important transient intermediates while comparison of a series of structurally related molecules is a powerful means of inferring the key factors that control reaction selectivity and energetics. Surface spectroscopies, such as X-ray photoelectron, high-resolution electron energy loss, and near-edge X-ray absorption fine structure, are important in defining the structure and chemical nature of

nonvolatile surface species and in defining the energetics of bond-breaking processes yielding nonvolatile products.

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**Registry No.** Trimethylene sulfide, 287-27-4; tetrahydrothiophene, 110-01-0; ethanethiol, 75-08-1; 1-propanethiol, 107-03-9; 1-butanethiol, 109-79-5; 1-pentanethiol, 110-66-7; benzenethiol, 108-98-5; molybdenum, 7439-98-7.

## In Search of Carbene Ion Radicals in Solution: Reaction Pathways and Reactivity of Ion Radicals of Diazo Compounds

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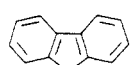
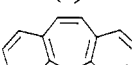
In the period of just over 100 years since the first was prepared,<sup>1</sup> aliphatic diazo compounds, RR'CN<sub>2</sub>, have been involved in many important developments in structural organic chemistry, organic synthesis, and the study of organic reaction mechanisms.<sup>2</sup> A feature of their chemistry is the diversity of reactive intermediates that can be generated by removal of a molecule of nitrogen under various experimental conditions. Perhaps the simplest of such processes is the thermolytic or photolytic cleavage of the C-N bond, which gives rise to carbenes, RR'C:, a field of revitalized activity in recent times.<sup>3</sup> Proton transfer to diazo compounds yields diazonium (RR'CHN<sub>2</sub><sup>+</sup>) and carbenium ions (RR'CH<sup>+</sup>), while Lewis acids lead to organometallic analogues. Nitrogen loss by attack of nucleophiles on the diazo function is much less common, but hydride transfer has been reported to give rise to carbanions (RR'CH<sup>-</sup>) in favorable cases.<sup>4</sup> This Account is concerned with the behavior of diazo compounds in fluid solution when subjected to one-electron reduction or oxidation. For the most part we shall deal with situations in which the initial electron transfer takes place at an electrode, although chemical one-electron oxidizing and reducing agents can also be used.

Aliphatic diazo compounds undergo one-electron oxidation and reduction in solution at readily accessible potentials.<sup>5</sup> The data in Table I are a representative

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**Table I**  
Redox Potentials of Selected Aliphatic Diazo Compounds RR'CN<sub>2</sub>

R	R'	$E_{1/2}(\text{ox})/\text{V}^{a,b}$	$E^p(\text{red})/\text{V}^{a,c}$
H	H	1.70 <sup>d</sup>	
EtO <sub>2</sub> C	H	2.10 <sup>d</sup>	
EtO <sub>2</sub> C	EtO <sub>2</sub> C		-1.33 <sup>g</sup>
EtO <sub>2</sub> C	Ph	1.43 <sup>e</sup>	
Ph	Ph	0.95 <sup>d</sup>	-1.71 <sup>h</sup>
Ph	PhCO	1.48 <sup>e</sup>	-1.12 (CH <sub>3</sub> CN) <sup>i</sup>
		1.22 <sup>d</sup>	-1.35 <sup>j</sup>
		0.77 <sup>f</sup>	

<sup>a</sup> Corrected to SCE. <sup>b</sup> Rotating Pt disk electrode in CH<sub>3</sub>CN solution. <sup>c</sup> Cyclic voltammetry on 1-5 mM solutions of the diazo compound in DMF; potential scan rate ca. 100 mV s<sup>-1</sup>; glassy carbon or Pt working electrode. <sup>d</sup> Reference 6. <sup>e</sup> Reference 7. <sup>f</sup> Reference 8. <sup>g</sup> Reference 9. <sup>h</sup> Reference 10. <sup>i</sup> Reference 11. <sup>j</sup> Reference 12.

selection of reported values. It should be remembered that the redox processes to which these potentials refer

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