Chemical Reviews

Volume 92, Number 4 June 1992

Model Studies of the Desulfurization Reactions on Metal Surfaces and in Organometallic Complexes

BENJAMIN C. WIEGAND and CYNTHIA M. FRIEND*

Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138

Received September 20, 1991 (Revised Manuscript Received January 27, 1992)

Contents

1. Introduction

The study of the reactions and bonding of sulfur-containing molecules is a field of wide importance and growing interest. Due to their importance in hydrodesulfurization catalysis, in forming metal–sulfur linkages in biological systems, in electrode chemistry, in forming self-assembled monolayers, and in organic synthetic routes, the field of sulfur reactions is continuing to expand. Desulfurization reactions induced by metals will be the focus of this review.

TABLE I. Electron Energy Loss Assignments for *tert*-Butanethiol

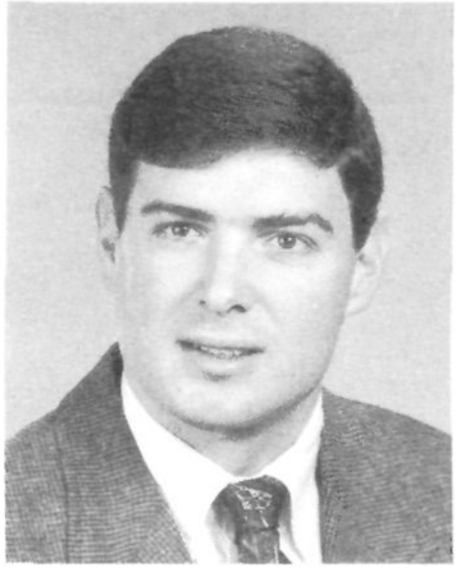
tert-butanethiol, cm^{-1}	*tert*-butanethiolate, cm^{-1}	gas phase, cm^{-1}	assignments
2935	2930	2950	ν(C–H)
2525	–	2565	ν(S–H)
1440	1440	1450	$\delta_a(CH_3)$
	1380	1370	$\delta_s(CH_3)$
1180	1180	1180, 1210	ν_a(MeCMe),$\rho(CH_3)$
915	915	930	$\rho(CH_3)$
–	800	820	ν(C–C)
600	575	587	ν(C–S)
	376	295	δ(CCS)
310	265	235	$\tau(CH_3)$

A considerable amount of attention has been given to defining the reaction mechanisms involved in the hydrodesulfurization of petroleum feedstocks, due to their vast importance and widespread application in industry.[1] The basic hydrodesulfurization process consists of passing a sulfur-containing molecule over a catalyst in the presence of hydrogen and is

$$C_xH_yS + nH_2 \rightarrow \text{hydrocarbons} + H_2S$$

The catalyst generally used in hydrodesulfurization consists of a molybdenum disulfide phase, MoS_2, promoted by the addition of either cobalt or nickel.[2] Other metals such as Os, Rh, Ir, and Ru are known to be better catalysts, but due to the availability and lower cost of Mo, it is the catalyst of choice in industrial applications. In spite of its industrial importance, there are many things still unknown about the catalyst. The active phase of the catalyst has been dubbed a Co–Mo–S phase in which the Co atoms are at the edges of MoS_2 crystals.[2-5] However, the active site of the catalyst is still unknown. The effect of the catalyst support, alumina or activated carbon, also plays a pronounced role on hydrodesulfurization activity and

0009-2665/92/0792-0491$10.00/0



Benjamin Carl Wiegand was born and raised in Urbana, IL. He received his B.S. in chemistry from the University of Illinois in 1986. He subsequently earned his A.M. in 1988 and his Ph.D. in 1991 in Chemistry from Harvard University. He is known for his work on the mechanisms of surface reactions involving heteroatom removal on single crystal metal surfaces under ultrahigh vacuum conditions. In 1989, he received the Morton Traum Student Award in Surface Science in recognition of his work. He is presently a Postdoctoral Associate in the Materials Science department at the University of Illinois and intends to pursue a career in academia.

Cynthia Friend is recognized for her research studying complex reactions occurring on solid surfaces. Her work places emphasis on defining the mechanism of reactions important in semiconductor device fabrication and heterogeneous catalysis. She uses a combined chemical and spectroscopic approach in order to fully understand surface processes on a molecular level. Analogy with organometallic chemistry is relied upon to establish principles governing coordination and bond activation on surfaces. Her repertoire of experimental methods includes near-edge X-ray absorption fine structure (NEXAFS), quantitative Auger electron spectroscopy, X-ray photoelectron spectroscopy, multiple internal reflection Fourier transform infrared spectroscopy, and high-resolution electron energy loss spectroscopy. She has received several honors recognizing her research. Her honors include the 1991 Garvan Medal of the American Chemical Society, the 1991 Iota Sigma Pi Agnes Fay Morgan Research Award in Chemistry, the 1990 Distinguished Young Alumna Award-University of California, Davis, a Union Carbide Innovation Recognition Award in 1988–89, an NSF Presidential Young Investigator Award in 1985, and an IBM Faculty Development Award for the period 1983–1985. She was also the 1991 Lucy Pickett Lecturer at Mount Holyoke College, is the 1992 Cargill Lecturer at the University of South Florida, and is a 1992 Welch lecturer. In addition to her research, Prof. Friend is actively involved in teaching and in the process of encouraging young women to pursue a career in science. She is a current member of the Board of Trustees, Radcliffe College, and a member of the NSF Chemistry Advisory Panel.

selectivity and is under investigation.[6]

Although the petroleum feedstocks contain an assortment of thiols, cyclic sulfides, and thiophenes,[7] most of the work has centered on the thiophenic compounds. Since thiophenes are the most difficult of the sulfur-containing molecules to desulfurize due to aromatic stabilization, most of the studies of developing catalysts have dealt with the reactions of thiophenes. Numerous studies of thiophene desulfurization have been performed on transition metal surfaces, as well as in organometallic complexes. Even in the specific case of thiophene, the exact mechanism of thiophene hydrodesulfurization to form a mixture of butenes, butane, and butadiene is not well understood.

2. The Cluster-Surface Analogy as Applied to Hydrodesulfurization Catalysis

Various approaches have and are being employed to more fully understand the mechanism for the hydrodesulfurization of sulfur-containing molecules. One approach is to study these reactions under actual reaction conditions using high surface area catalysts. The complexity of the catalyst material and the possible contribution of highly active minority sites renders it impossible to study mechanisms on a molecular level under actual catalytic conditions. Furthermore, there are very few spectroscopic methods available to probe surface species in situ under realistic conditions.

Studies of the reactions on highly ordered single-crystal metal surfaces or in structurally characterized discrete metal clusters have been undertaken in order to simplify the study of the sulfur-extrusion process. In these cases, a well-defined system is employed which can be studied in detail to learn more about reaction intermediates and pathways, with the hope that this knowledge can be transferred to the actual catalyst system.

2.1. Comparison of Surface Chemistry and High Surface Area Catalysis

The modeling of the hydrodesulfurization of sulfur-containing molecules on catalysts by studying the related desulfurization process on single-crystal metal surfaces has received considerable attention. The complex structure of the catalyst surface can be modeled as a collection of minute single crystals. The properties of the single-crystal surfaces, crystal orientation or the presence of steps or kinks, can then be varied systematically to model the catalyst and to specifically define the sensitivity of the desulfurization reaction on the metal atom geometry. For example, monitoring the desulfurization reaction of sulfur-containing molecules on surfaces with different structures, enables one to model the effect of surface structure in a controlled fashion. Similarly, the effect of chemical adsorbates on desulfurization kinetics can be followed by adding surface adsorbates, such as sulfur, carbon, cobalt, and hydrogen.

There are clearly several significant differences between studies of single-crystals under ultrahigh vacuum conditions and high surface area catalysts under higher pressure conditions. The pressure regimes are dramatically different; 10^{-10} Torr for ultrahigh vacuum studies and pressures ≥ 760 torr in actual catalytic conditions. Secondly, the reactions take place on distinctly different substrates. In ultrahigh vacuum conditions, reactions occur on a ~ 1 cm^2 disk, while in catalytic situations, metals are often dispersed on high surface area oxide supports (~100–200 m^2/g).[8] The metal particles in high surface area catalysts are probably sufficiently large that the single crystals are a good model. Care must be taken when applying concepts derived from ultrahigh vacuum studies to higher pressure conditions to account for the "pressure gap", but there are several examples where this has been successfully done.[9,10]

A main advantage of ultrahigh vacuum conditions is that a variety of surface-sensitive tools are available to probe the surface, including Auger electron, high-resolution electron energy loss, temperature-programmed reaction, and X-ray photoelectron spectroscopies, low-energy electron diffraction, and near-edge X-ray absorption fine structure. Temperature-programmed reaction spectroscopy is used to measure reaction kinetics, as well as determine reaction products. Auger electron and X-ray photoelectron spectroscopies determine the composition of the surface at various stages of reaction. X-ray photoelectron spectroscopy also provides important information about the nature of species on the surface and is specifically used to determine the conditions necessary for C–S bond breaking. High-resolution electron energy loss, in conjunction with X-ray photoelectron spectroscopy, identifies surface intermediates and in some cases provides structural information. Low-energy electron diffraction is used to evaluate the degree of long-range order of metal surfaces with and without added surface adsorbates. Near-edge X-ray absorption fine structure is used for determining orientation of species that can be isolated on the surface. Such structural information is particularly important for theoretical modeling of the bonding of surface intermediates. These spectroscopic tools complement each other and must be used in conjunction with other methods to fully understand a reaction mechanism. Chemical probes, such as isotopic labeling and temperature-programmed reaction spectroscopy when other surface species are present, are also used to enhance the power of these tools. Mass spectrometry is used to identify gas-phase reaction products because of its high sensitivity and compatibility with ultrahigh vacuum conditions. Since the surface area of a single crystal is only on the order of 1 cm^2, only ~10^{14}–10^{15} molecules are produced during a reaction.

As an example of the capability of the surface spectroscopic tools, the identification of the intermediates formed during reaction of *tert*-butanethiol on Mo(110) are described.[11] X-ray photoelectron and high-resolution electron energy loss spectroscopies *together* confirm the presence of *tert*-butanethiolate as the sole intermediate on the surface up to hydrocarbon formation temperatures.

X-ray photoelectron data were taken of condensed *tert*-butanethiol and used as a reference state (Figure 1a). There is one sulfur species on the surface with $S(2p_{3/2})$ and $S(2p_{1/2})$ binding energies of 163.4 and 164.6 eV.[12] There is a broad asymmetric C(1s) spectrum that is best fit with two peaks at 285.8 and 284.9 eV in a ratio of 1:3; the peak at 285.8 eV is assigned to the carbon bound to the sulfur, while the peak at 284.9 eV is assigned as the other three equivalent carbons.

There is a single intermediate detected on the surface in X-ray photoelectron data when *tert*-butanethiol is exposed to Mo(110), which is identified as a surface *tert*-butanethiolate (Figure 1b). The S(2p) binding energies are 162.6 and 163.8 eV, in good agreement with those reported previously for thiolates on Mo(110).[13,14] They are clearly different than those of atomic sulfur, 161.3 and 162.5 eV (Figure 1d).[13]

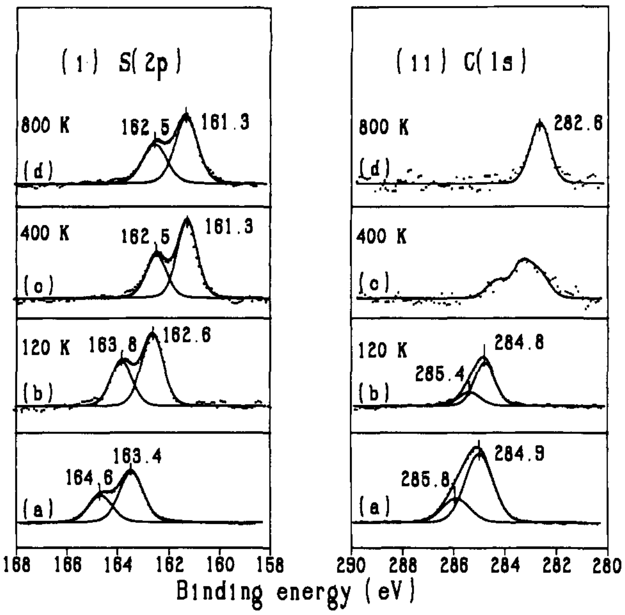


Figure 1. (i) S(2p) and (ii) C(1s) X-ray photoelectron spectra of (a) *tert*-butanethiol multilayers and a *tert*-butanethiol monolayer annealed to (b) 120 K, (c) 400 K and (d) 800 K (reprinted from ref 11; copyright 1992 American Chemical Society).

C(1s) photoelectron data are also consistent with the presence of a *tert*-butanethiolate intermediate. Again, a broad asymmetric spectrum is seen that is best fit with two peaks at 285.4 and 284.8 eV in a ratio of 1:3. These data are in agreement with an intact *tert*-butyl hydrocarbon skeleton in the intermediate. The data is not consistent with the presence of adsorbed hydrocarbon intermediates on the surface, as these would be expected to have binding energies of ~283–284 eV.[15]

The S–H bond of *tert*-butanethiol is broken upon adsorption at 120 K on the basis of vibrational data (Figure 2b, Table I). Electron energy loss was chosen as the vibrational probe because of its high sensitivity. Electron energy loss data of condensed *tert*-butanethiol were taken and used as a reference state (Figure 2a). Importantly, a loss due to the ν(S–H) mode at 2525 cm^{-1} is seen in the condensed thiol spectra. However, for coverages less than or equal to a monolayer, the ν(S–H) mode is absent and all other features remain essentially the same as for the condensed thiol (Figure 2b). The absence of the S–H stretch demonstrates that this bond is broken when *tert*-butanethiol is exposed to the Mo surface.

Annealing the surface to temperatures past hydrocarbon formation (400 K) produces atomic sulfur and hydrocarbon fragments on the surface (Figure 1c). There are two S(2p) peaks at 161.3 and 162.5 eV in good agreement with binding energies expected for atomic sulfur. C(1s) data evidence a peak at ~283 eV, again in good agreement with expected binding energies for hydrocarbon fragments. Further annealing to 800 K results in the presence of atomic carbon and sulfur on the surface (Figures 1d and 2c). Only ν(metal–S) and ν(metal–C) modes are seen in the electron energy loss

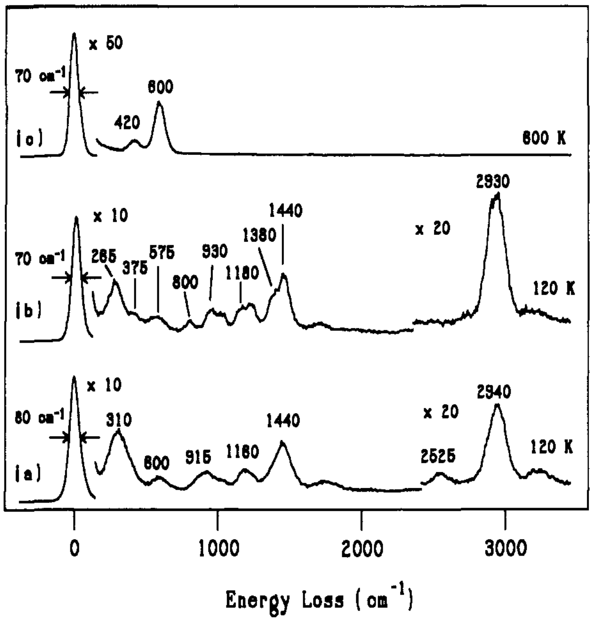


Figure 2. High-resolution electron energy loss spectra of (a) *tert*-butanethiol multilayers at 120 K, (b) *tert*-butanethiol monolayers at 120 K, and (c) *tert*-butanethiol multilayers annealed to 800 K (reprinted from ref 11; copyright 1992 American Chemical Society).

spectra of *tert*-butanethiol annealed to 800 K; no losses attributable to ν(C–C) or ν(C–H) modes were seen.

There are fewer spectroscopic methods available which can probe reactions under higher pressure conditions, since electron spectroscopies cannot be used. The catalyst surface is often analyzed ex situ using electron spectroscopies, such as X-ray photoelectron spectroscopy, however. Reaction products can be analyzed using gas chromatography because of the high surface area. Mass spectrometry is also sometimes used on samples of the gas in the reactor. Infrared spectroscopy is the primary tool for probing the catalyst surface during reaction since it is compatible with the higher pressures. Polarization modulation can be used to eliminate the contribution of the gas phase and specifically study surface intermediates. The heterogeneity of the catalyst sample often renders interpretation of the infrared data difficult, however. Peaks due to different species are often not resolved even for simple diatomics such as CO. Overall, it is not possible to identify surface species on high surface area materials in detail.

2.2. Comparison of Organometallic Chemistry with Surface Chemistry

Inorganic and organometallic chemists have used their ability to synthesize discrete metal clusters with sulfur-containing molecules in different binding sites and coordination geometries, in an effort to model early stages of the hydrodesulfurization process. The binding of molecules on extended metal surfaces and in clusters are thought to be similar suggesting that the bonding of molecules to metals is primarily a localized phenomena based on both experimental and theoretical studies.[16-19] The primary advantages of studying discrete clusters or complexes are that their structures are readily characterized and that theoretical modeling is simplified since there are fewer atoms than on an extended surface.

Since hydrodesulfurization reactions take place on a Co- or Ni-promoted MoS_2 surface, most of the studies have been performed with clusters of these metals. Other related metals, such as osmium, ruthenium, and tungsten as well as vanadium, niobium, and tantalum are also under intense study. The ability to make discrete bimetallic clusters is an effective way to model hydrodesulfurization catalysts since a variety of different environments involving Co, Mo, and S can be built in order to systematically study the effect of coordination site on bonding and reactivity.

Once these metal clusters are formed, their reactions and intermediates are amenable to study, with a wide variety of spectroscopic techniques used in an effort to learn more about mechanistic detail. These compounds are typically characterized by nuclear magnetic resonance, Fourier transform infrared spectroscopy, Raman spectroscopy, and X-ray crystallography. With the aid of these spectroscopies, atom positions, bond strengths, bond lengths, and coordination types of the starting molecules and further reaction intermediates are determined by these methods. An additional benefit of this approach is the ability to follow the reactions of specific intermediates under reaction conditions.

Discrete metal clusters may differ from catalysts in several important ways. First of all, it may not be possible to synthesize the desired intermediates. For example, only until very recently have thiophenic reaction intermediates been synthesized. Intermediates that contain both thiolates and hydrides have also only been synthesized in the last year or two. Furthermore, there may be significant differences in the types of ligand binding in metal clusters and on a surface. The bonding of ligands is often affected by other ligands on the same metal center due to both electronic and steric effects. Since the same environment is not present on a surface, in general, there are several examples of bonding in complexes that are not possible on surfaces. For example, there are several recent examples of ring compounds that bind to two different metals on different faces of the ring. Also, the varying oxidation states of the metal in the clusters can also lead to different chemistry. In this regard, the effect of oxidation state in high-surface area catalysts can be modeled effectively, but the cluster-surface analogy may break down for extended surfaces. Differing degrees of coordinative unsaturation on extended surfaces and in clusters may also lead to differences in reactivity. Extended metal surfaces are highly coordinatively unsaturated and there are typically several adjacent coordination sites. These surface structures may not be available in a discrete cluster.

In spite of these differences, there has been a recent upsurge in the synthesis of metal clusters as models for catalysts. The synthesis of clusters with unusual bonding has opened new doors for catalyst design and it is, thus, a burgeoning field.

3. *Scope of This Review*

This review will focus on model studies of the related desulfurization reactions of cyclic sulfides and thiols under ultrahigh vacuum conditions on single-crystal metal surfaces. A direct comparison of the reactions of the same compounds in organometallic complexes will be made, where appropriate, and possible parallels

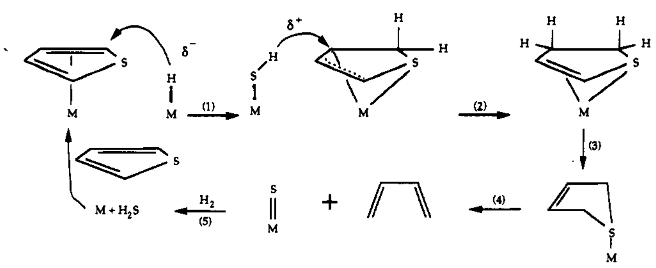


Figure 3. Proposed mechanisms for thiophene hydrodesulfurization (reprinted from ref 38; copyright 1987 American Chemical Society).

in the two fields will be examined. As mentioned before, the reactions of molecules with thiophenic functionalities have been a central topic of research in this field. However, their reactions have been central topics in reviews of desulfurization on metal surfaces[20] and in organometallic complexes,[7,21] so only a brief summary and very recent results of the reactions of these compounds on single-crystal metal surfaces and in organometallic complexes will be given here. This review is intended to cover the study of the literature on the mechanism for thiol desulfurization over the last 5 years. Specifically, desulfurization of thiols used in synthetic procedures, and catalyst studies, where catalyst structure was the main concern, are not covered here. Due to the vastly growing field, we apologize for any of the many excellent papers overlooked in this review.

4. Thiophene

The reactions of thiophene and related molecules have been the most widely studied compounds in efforts to understand the hydrodesulfurization mechanism. There have been three basic models proposed for the hydrodesulfurization reaction (Figure 3). In one scheme, hydrogenation of the thiophene ring to form a 2,3-dihydrothiophene intermediate is the first step.[22] Nucleophilic attack at the 2-position by a hydride has been specifically proposed as the first step, on the basis of model studies of homogeneous transition metal complexes.[7] Alternatively, hydrogenolysis of the carbon–sulfur bonds may occur directly, forming 1,3-butadiene.[23] Finally, thiophene desulfurization may proceed without hydrogen via β-hydrogen elimination to produce diacetylene which would be subsequently hydrogenated.[24] A fourth proposal has been recently presented which involves C–S bond cleavage of the thiophene before hydrogenation via bonding of the thiophene to two metal centers.[25]

In an effort to learn more about the hydrodesulfurization reaction, the combination of model organometallic and surface studies has been undertaken. The study of thiophene on surfaces has centered on its binding geometry and further reactivity. On the other hand, the ability to synthesize thiophene in different binding modes has only been possible recently,[21] so that giant strides are being made. As mentioned previously, only a brief review of the work will be given here, and we refer the readers to excellent reviews on the subject.[7,20,21]

A rich variety of different binding geometries have been accessed for thiophene bound in organometallic complexes (Figure 4).[21] η^1,*S*-Bound,[7,26-28] η^4-bound,[29-32] η^5-bound,[29,33-42] η^4,*S*-μ_2-bound,[25,31,43,44] η^4,*S*-μ_3-bound,[25,45] and η^2-bound[46] geometries have all been reported. A wide variety of binding geometries of the thiophene intermediates are available via synthetic routes, so that attention can now be placed on investigating the reactivity of these complexes.

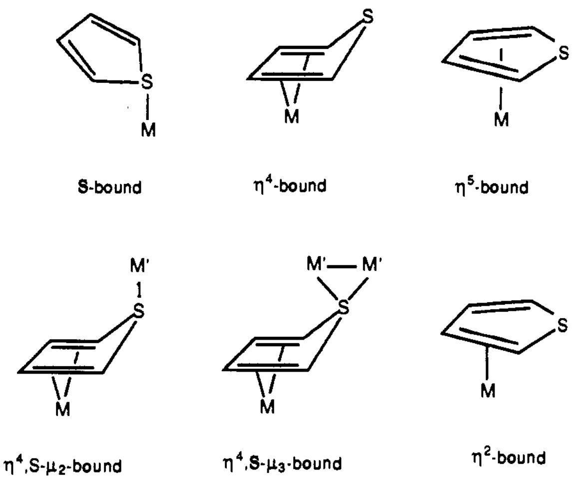


Figure 4. Known coordination geometries of thiophene in organometallic complexes (reprinted copyright 1990 Elsevier Science Publishers, B.V.).

Early studies of thiophene desulfurization found that an η^5-coordination of the thiophene in the clusters mimicked the activity and selectivity for H–D exchange in thiophene over actual catalysts. Selective exchange of the C–H bonds adjacent to sulfur in thiophene was observed for high surface area MoS_2 catalysts and for η^5-coordinated thiophene in a ruthenium thiophene complex. In fact model studies of Mn,[41,42] Ru,[36,37,39] and Fe[42] complexes all exhibit similar reactivity.

Calculations modeling the interaction of thiophene with molybdenum clusters show that there is weakening of the C–S bond at the positions α to sulfur in a η^5-bound thiophene, but not in a η^1,*S*-bound thiophene complex.[47] Ring opening of the thiophene intermediate has been seen to occur at the α-position by nucleophilic attack of a hydride.

Recently, coordination of the thiophene through the sulfur has been intensely investigated. Most of the early η^1,*S*-bound complexes were only weakly bound and were easily displaced, in contrast to surface studies where desulfurization to atomic constituents took place. However, recent results show that η^1,*S*- and η^4-coordination can lead to metal insertion into the C–S bond, which is important in the pathway for thiophene desulfurization (Figure 5).[25,43,48] In fact, η^4-coordination of the thiophene made the sulfur more basic and also led to sulfur adducts that were tightly bound.

In spite of the intense effort in studying the reactions of thiophene in organometallic complexes, desulfurization of thiophene to form gas-phase products has not been observed. The reaction of thiophene with $Fe_3(CO)_{12}$ produced FeS and $Fe_2(CO)_6(C_4H_4)$ in low yields, however.[49]

Hydrogenation products have only been seen during thiophene reaction on a few surfaces under ultrahigh vacuum conditions. Butadiene is formed from thiophene reaction on Pd(111),[50] Pt(111),[51,52] and Rh(111).[53] Various hydrocarbons are also seen from the reaction of thiophene on Ni(111)[54] and W(211).[55] Interestingly, all of these surfaces are known hydrogenation catalysts, so it appears that the ability to facilitate C–H bond

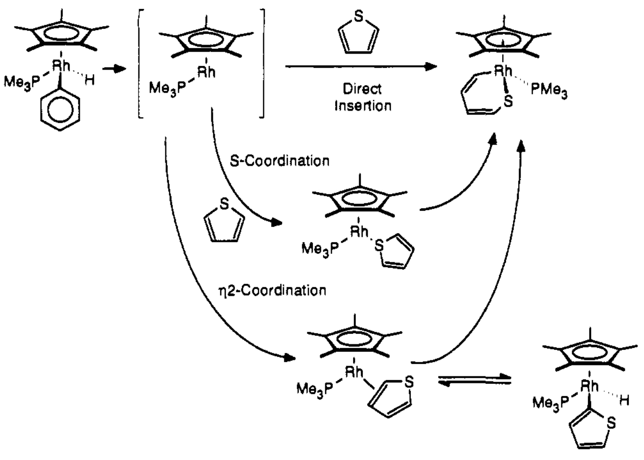


Figure 5. Proposed mechanism for an η^1-sulfur bound rhodium thiophene complex (reprinted from ref 48; copyright 1991 American Chemical Society).

formation is important. The lack of hydrogenation activity under ultrahigh vacuum conditions is almost certainly a direct result of the low hydrogen pressure. Under higher pressure conditions, the steady-state hydrogen concentration would be higher on the surface and the hydrogenation yields on all surfaces studied are expected to increase.

The reactions of thiophene have also been studied on Re(0001),[56] Mo(100),[57] Mo(110),[58] and Ru(0001).[59] The reaction of thiophene on these surfaces results mainly in nonselective decomposition to atomic sulfur and carbon and gaseous dihydrogen. The presence of nonselective decomposition makes determination of a detailed mechanism difficult, although formation of metallacycle intermediates have been proposed.[59,60] No activation of thiophene is seen from the reaction on Cu(100).[61]

The initial binding geometry of thiophene, important in cluster desulfurization of thiophene, does not correlate with reactivity on extended metal surfaces. For example, thiophene is tilted on Pt(111)[51] but nearly parallel to Rh(111)[53] even though thiophene desulfurizes to butadiene on both surfaces. No hydrogenated thiophene intermediates were isolated in these studies, although the mechanistic details were not mapped.

The orientation of thiophene with respect to metal surfaces is sensitive to its coverage and the coverage of coadsorbed hydrocarbons and sulfur. On most surfaces, a parallel geometry is favored at low coverage and a more perpendicular disposition of the ring is favored at high coverage. The exceptions are Rh(111)[53] and Cu(111)[62] for which there are parallel geometries at all coverages studied. These coverage-dependent phenomena are probably due to intermolecular interactions and would be analogous to steric interactions with neighboring ligands in a discrete cluster or complex.

The reactions of partially hydrogenated thiophenes have also been studied in an effort to probe for intermediate steps involving ring hydrogenation. Even though the hydrogenation of thiophene has not been observed under ultrahigh vacuum conditions, the possibility of ring hydrogenation must be considered since the pressure of H_2 is considerably higher under actual catalytic conditions. Furthermore, the reactivity of 2,5-dihydrothiophene has been studied in complexes so that this serves as a good point of comparison for the reactivity of surfaces and clusters. In complexes, hydrogenation of thiophene to form 2,3-dihydrothiophene has been proposed to be the initial step in thiophene hydrodesulfurization.[7,25] The 2,3-dihydrothiophene intermediate is proposed to readily isomerize to the more stable 2,5-dihydrothiophene intermediate which eliminates butadiene. In light of this, the reaction of 2,5-dihydrothiophene was studied on Mo(110).

Butadiene is produced during temperature-programmed reaction of 2,5-dihydrothiophene on Mo(110).[63] Dihydrothiophene intramolecularly eliminates butadiene with ~70% selectivity. The kinetics for butadiene elimination are very rapid but depend on the presence of sulfur.

The reactivity of 2,5-dihydrothiophene is very similar on Mo(110) and in complexes. These results indicate that desulfurization of partially hydrogenated rings is facile and that hydrogenation may precede C–S bond breaking during thiophene reaction under appropriate conditions. On Mo(110), no hydrogenation products are seen during thiophene desulfurization. This is probably due to a combination of the low hydrogen pressure and the low hydrogenation activity of Mo, both of which will render hydrogenation slow. Gaseous butadiene is directly eliminated from 2,5-dihydrothiophene with very high selectivity on Mo(110)[63] and Mo(110)–p(4×1)–S.[64] Butadiene formation from 2,5-dihydrothiophene occurs in a direct intramolecular elimination reaction, whereas hydrocarbon production from thiophene requires hydrogenation. A minimum of two C–H bonds must be formed to make butadiene from thiophene, for example. Interestingly, butadiene formation is also seen from reaction of 2,5-dihydrothiophene and of thiophene on Rh(111).[53,65] These results suggest that 2,5-dihydrothiophene may be an intermediate in the desulfurization of thiophene on Rh(111) even under ultrahigh vacuum conditions. The higher hydrogenation activity of Rh would account for the rapid ring hydrogenation.

4.1. Comparison of Thiophene on Metal Surfaces and in Clusters

There are many parallels in the reactions and bonding of thiophenes on metal surfaces and in clusters. Both η^1,*S*- and η^5,π-bound thiophenic intermediates were shown to be important adsorption geometries in both surfaces and in clusters. In fact, the observation of sulfur-bonded thiophene on surfaces led to the intense search for these intermediates in organometallic clusters. The importance of hydrogen in thiophene desulfurization was also demonstrated for both cases. Hydrocarbon products are only seen on metal surfaces with high hydrogenation capabilities. Hydrocarbon formation from 2,5-dihydrothiophene and *not* from thiophene on Mo(110) further supports the proposal that hydrogen is important in the desulfurization. Likewise in organometallic clusters, the reactions of hydride sources with thiophenic bound clusters were seen to promote C–S cleavage.

The primary differences between the desulfurization studies of thiophene on metal surfaces and in clusters are the absence of desulfurization products produced from reactions induced by clusters and the difficulty in isolating structural intermediates on metal surfaces. Butadiene formation is seen on a number of surfaces,[20,50–53] while hydrocarbon formation is not generally seen in cluster reactions. On the other hand, the

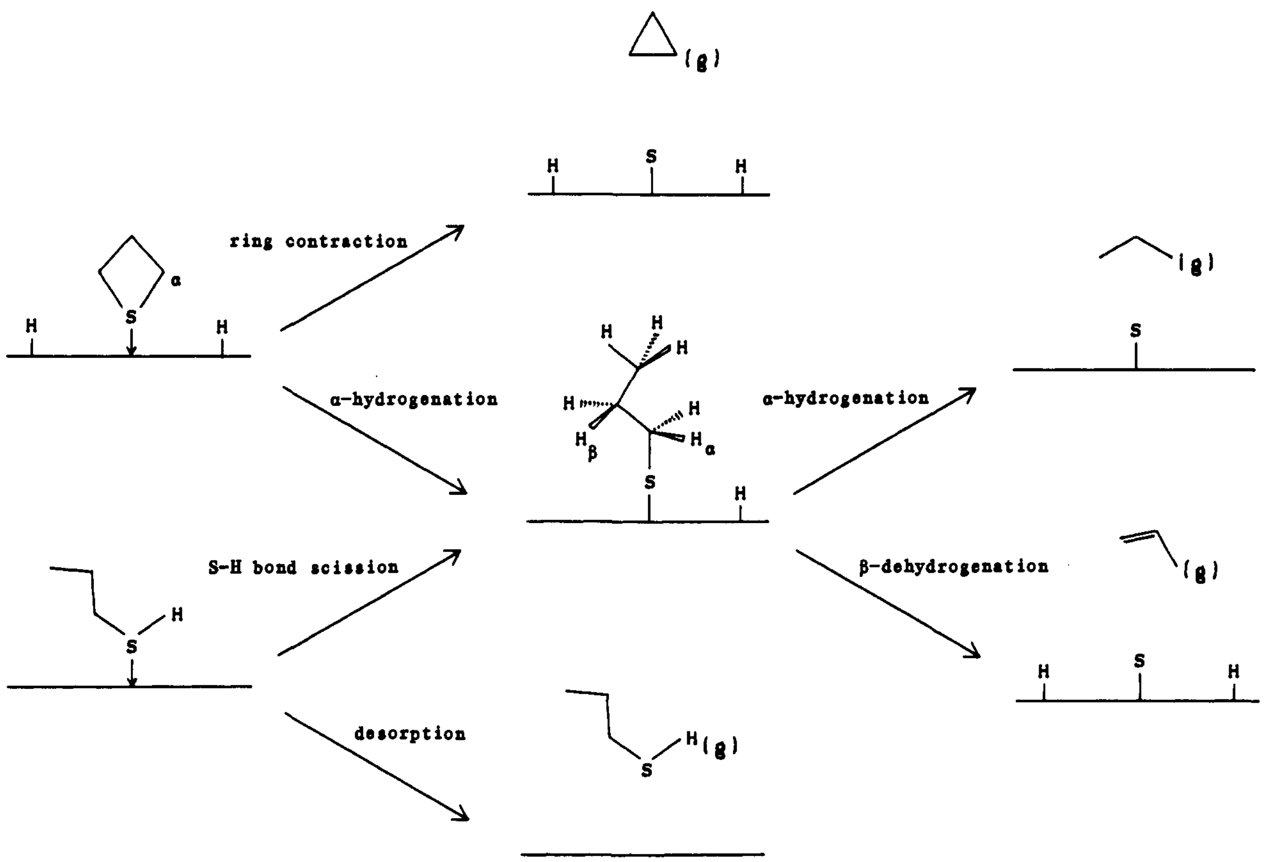


Figure 6. Proposed mechanism for thietane desulfurization on Mo(110) (reprinted from ref 85; copyright 1987 American Chemical Society).

butadienethiolate[40,66] and ferrole[49] intermediates have been isolated in organometallic complexes. No intermediates have been unequivocally identified, although metallacyclic structures have been proposed for the reactions of thiophene on metal surfaces.

Recently, the synthesis of thiophene coordinated to multiple metal centers on opposite faces of the ring has raised the possibility of unique chemistry in clusters.[25,31,43-45] These binding configurations would be unaccessible on the surface, so that inherent differences in the two regimes will curtail comparison between them.

5. Cyclic Sulfides

5.1. Cyclic Sulfides on Mo(110)

The reactions of cyclic sulfides have been under intense investigation, mainly on Mo(110). Since hydrogenation of thiophene intermediates may be important in hydrodesulfurization and are components of feedstocks themselves, understanding the reactivity of cyclic sulfides on surfaces is important.

The size and amount of ring strain in the cyclic sulfides were varied on Mo(110) in an effort to learn more about their effects on cyclic sulfide desulfurization kinetics. Four channels were available during desulfurization: ring opening to form a thiolate followed by decomposition to alkane and alkene; intramolecular elimination; nonselective decomposition to atomic carbon and sulfur and gaseous dihydrogen; and molecular desorption. Figure 6 shows the reaction mechanism for a particular cyclic sulfide, thietane, which has three channels available to it. Table I shows the available channels observed for the C_2–C_5 cyclic sulfides.

The amount of ring strain governs the kinetics of ring opening of the cyclic sulfides to form the corresponding thiolates on Mo(110). Thiolate formation was reported for all cyclic sulfides studied, except for the C_2 sulfide, thiirane. For example, ring opening of the highly strained C_3 sulfide, thietane, led to propanethiolate formation on Mo(110). The propanethiolate intermediate then underwent competing C–S bond hydrogenolysis to form propane and C–S and C–H bond scission to form propene. Hydrocarbons were also formed in the reactions of tetrahydrothiophene and pentamethylene sulfide, which produced butane and butene and pentane and pentene, respectively. In fact, ring opening of pentamethylene sulfide to form pentanethiolate was proposed to be the rate-limiting step in pentamethylene sulfide desulfurization.

The selectivity and kinetics of hydrocarbon formation from the thiolate intermediate is dramatically influenced by the amount of surface hydrogen. The yield of hydrocarbon products, butane and butene, from tetrahydrothiophene reaction increases by a factor of 6 when a saturation coverage of surface hydrogen is present. Also, the temperature of butane formation was *decreased* by 115 K by a saturation coverage of hydrogen. Correspondingly, the rate-limiting step was proposed to be C–S bond hydrogenolysis of the tetrahydrothiophene ring. There is no external source of hydrogen available for ring opening of the cyclic sulfides on Mo(110). Hence, nonselective decomposition of the molecule is the only source of hydrogen available. In accordance, X-ray photoelectron spectra of pentamethylene sulfide multilayers annealed to 250 K, for example, showed that atomic sulfur and carbon were

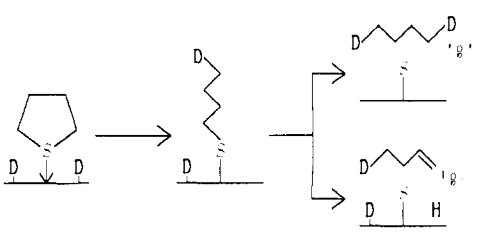


Figure 7. Reaction mechanism for deuterium incorporation into tetrahydrothiophene (reprinted from Friend, C. M.; Roberts, J. T. *Acc. Chem. Res.* 1988, *21*, 394; copyright 1988 American Chemical Society).

present, indicating that nonselective decomposition had occurred.[67] However, by preadsorbing surface hydrogen on the surface, the kinetics for ring opening are increased relative to nonselective decomposition, and the amount of hydrocarbon formation is increased.

The importance of a thiolate intermediate during cyclic sulfide desulfurization is further supported by studies of their decomposition in the presence of coadsorbed deuterium (Figure 7). A maximum of two deuteriums are incorporated into the alkane product formed, consistent with thiolate formation via ring opening and then a one-step hydrogenolysis to form the alkane. Importantly, only one deuterium is incorporated into the alkene product formed. This confirms that no reversible C-H(D) bond activation occurs.

The amount of ring strain was seen to control the formation of the intramolecular elimination product in cyclic sulfides. No intramolecular elimination product was detected in the reaction of the unstrained rings, tetrahydrothiophene (2 kcal/mol) and pentamethylene sulfide (0 kcal/mol). In contrast, ethylene and cyclopropane were formed from reaction of thiirane (18 kcal/mol) and thietane (19 kcal/mol), respectively.

The formation of ethylene from thiirane on Mo(110) via intramolecular elimination was calculated to occur with little activation energy.[68] Importantly, higher coordination binding sites of thiirane were energetically preferred over single-coordination sites. Binding of the thiirane in the higher coordination site led to weakening of the C-S bond and to formation of a second C-C bond, consistent with C-S bond weakening and formation of the C=C double bond upon adsorption. Similar results were also seen for the reaction of thietane on Mo(110).[68]

The third channel, molecular desorption, was also governed by the ring size and amount of ring strain. A fraction of the unstrained cyclic sulfides, tetrahydrothiophene and pentamethylene sulfide, molecularly desorb whereas 100% of the highly strained rings, thiirane and thietane, react. The activation energy for molecular desorption is not expected to vary dramatically for the different cyclic sulfides; only a small increase in the desorption temperature is anticipated as the molecular weight of the cyclic sulfide increases. Hence, the increase in the desorption yield for the unstrained rings must indicate a decrease in the kinetics for ring opening rendering molecular desorption competitive with ring opening. For the highly strained molecules, ring opening is considerably more rapid than desorption.

The fourth channel, nonselective decomposition to atomic carbon and sulfur and gaseous dihydrogen was seen for all cyclic sulfides studied. Nonselective decomposition is the sole source for thiolate hydrogenolysis to form alkanes. As the ring strain in the cyclic sulfide decreases, the kinetics of nonselective decomposition are more competitive with ring opening. This is borne out in the relative selectivity as a function of ring strain. The selectivities for the unstrained cyclic sulfides, pentamethylene sulfide (20%) and tetrahydrothiophene (25%), are much lower than the selectivities for thietane (45%) and ethylene sulfide (85%).

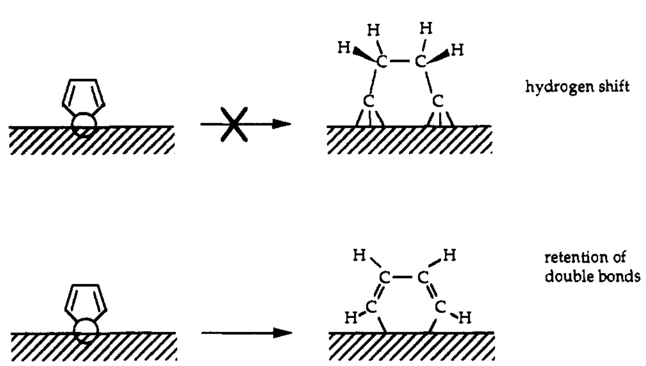


Figure 8. Possible intermediates formed during the reaction of tetrahydrothiophene on Pt(111) (reprinted from ref 52; copyright 1987 Elsevier Science Publishers B.V.).

5.2. Cyclic Sulfides on Other Surfaces

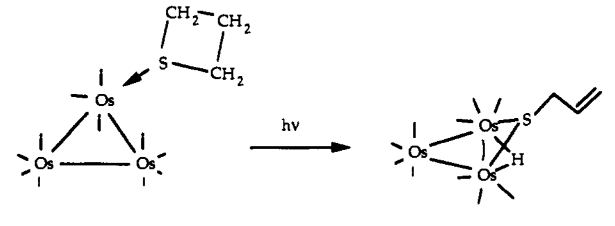
Although not as extensively studied, there are many similarities between the chemistry of cyclic sulfides on Mo(110) and that seen on other surfaces. For example, thiolate formation was proposed as the intermediate in tetrahydrothiophene desulfurization on W(211). It was proposed to subsequently react to form butane and butene. In contrast, no thiolate intermediate was seen for the reaction of tetrahydrothiophene formation on the faces of platinum single crystals; rather, a metallacycle is proposed (Figure 8).[52]

The release of ring strain in thiirane to form ethylene has also been seen before on other metal surfaces. Gaseous ethylene was observed during the reaction of thiirane on Rh(111),[65] while ultraviolet photoelectron spectra were consistent with ethylene formation on the Cu(110)[69] and Cu(100)[70] surfaces. Finally, molecular desorption was seen to be the dominant reaction channel for the reaction of the C_3–C_5 cyclic sulfides on Cu(110); no desulfurization was reported.[69]

5.3. Comparison to Organometallic Complexes

The reactivity of cyclic sulfides is very similar on surfaces and in clusters. Indeed, ring opening was also important in the reaction of cyclic sulfides in metal clusters.[71-73] Therefore, a similar dependence of desulfurization kinetics on the ring strain of cyclic sulfides is anticipated in clusters as for Mo. In fact, the same products were reported for the reaction of tetrahydrothiophene with WCl_6[74] as for Mo(110)[75] and W(211);[55] butane and butene were formed.[74] Likewise, the reaction of a thietane in an osmium cluster formed a 2-propene-1-thiolate via ring opening and β C–H bond scission, again similar to proposed intermediates for Mo(110) (Figure 9).[71,72]

The reactions of thiiranes and substituted thiiranes with metal clusters are similar to those on metal surfaces. For example, desulfurization of thiiranes has been observed with metal complexes of all of the metals



1 2

Figure 9. Reaction of thietane with osmium cluster (reprinted from ref 72; copyright 1990 American Chemical Society).

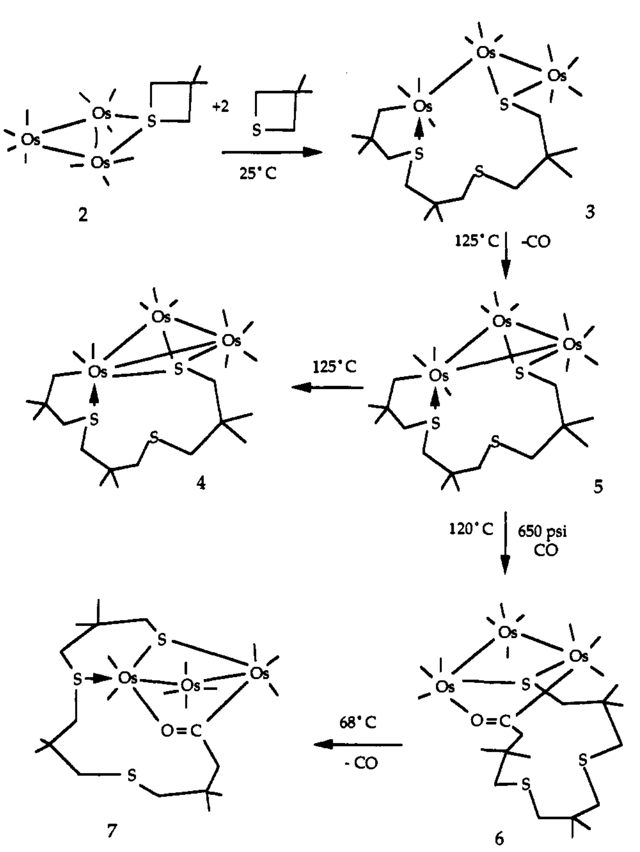


Figure 10. Proposed mechanism for thietane oligomerization in osmium cluster (reprinted from ref 82; copyright 1991 American Chemical Society).

used in hydrodesulfurization. Fe,[76] Mo,[77] Rh,[78] Os,[79,80] and bimetallic[81] complexes are all active desulfurization agents of thiiranes. Unfortunately, detailed mechanisms are not provided for most desulfurization reactions in these complexes, so that a comparison of reactive intermediates between the surfaces and the clusters is not generally possible.

A new pathway is seen for thietane reaction in metal clusters. Ring opening oligomerization of 3,3-dimethylthietane to form 11-osmo-2,2,6,6,10,10-hexamethyl-4,8-dithiaundecanethiolato was seen (Figure 10).[82] Importantly, oligomerization was only seen for thietane in a μ_2-bonding geometry; a mononuclear binding site for thietane produced no further reaction. Oligomerization was also seen in the reaction of thiirane with an osmium cluster.[83] In contrast, no oligomerization was seen during the reaction of thietane on Mo(110), where it is thought to bind in a polynuclear site. However, the low coverages of reactants and hydrogen pressure on single-crystal surfaces are not optimal conditions for oligomerization.[84] Some oligomerization has been proposed for the reaction of thiophene on Ni(111), but detailed mechanistic information was not obtained.[54]

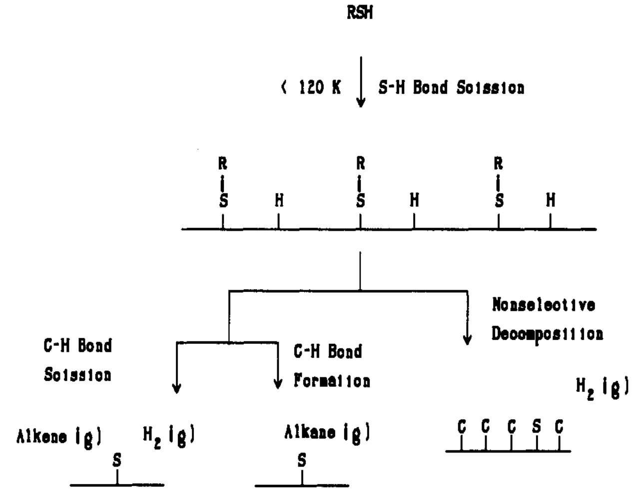


Figure 11. Mechanism for thiol desulfurization on Mo(110).

6. Thiols

The reactions of thiols on metal surfaces and in metal clusters have also led to significant understanding of the hydrodesulfurization mechanism. Due to the significance of the thiolate intermediate in cyclic sulfide desulfurization, a detailed understanding of its reactivity is important. Cleavage of the weak S–H bond of a thiol on a metal surface would be an ideal synthetic route to thiolates. In fact, methyl thiolate is formed from methanethiol on many different metal surfaces. More complex thiols were also studied on the Mo(110) surface, with comparative studies of thiols with different alkyl substituents leading to a detailed knowledge of the reaction mechanism, in particular the relative importance of C–S and C–H bond breaking and making processes.

6.1. Thiols on Mo(110)

In order to determine the mechanism for thiol reactions on metal surfaces, a systematic study of their reactivity on Mo(110) was performed. The C_2–C_5 primary thiols,[14,75,85,86] benzenethiol,[13] *tert*-butanethiol,[11] and 2-propene-1-thiol[87] were studied on Mo(110). Based on these results, a general mechanism was proposed to account for the reactivity of all thiols on Mo(110) (Figure 11). As seen in the reaction of cyclic sulfides, the thiolate intermediate was observed to be the kinetically important intermediate in thiol desulfurization on Mo(110).

The presence of the surface thiolate on Mo(110) has been confirmed by high-resolution electron energy loss and X-ray photoelectron spectroscopies.[11,13,14,86,87] The thiolate reacts via similar competing channels as seen for the cyclic sulfides: C–S bond hydrogenolysis to form the corresponding alkane; C–H and C–S bond scission to form the alkene; and nonselective decomposition to form atomic carbon and sulfur and gaseous dihydrogen. Molecular desorption was not observed during the reactions of thiols on Mo(110).

6.1.i. *tert-Butanethiol on Mo(110)*

tert-Butanethiol undergoes desulfurization on Mo(110) via the proposed mechanism to form alkane (isobutane) and alkene (isobutene) products. In order to determine which specific isomer was formed for both products, fragmentation patterns of the hydrocarbon products formed were quantitatively measured using an electron energy of 27 eV and compared to fragmentation patterns of authentic samples of the butane and butene isomers measured at 27 eV. Under normal operating conditions which utilize an electron energy of 70 eV, the mass spectra of the various isomers of butane and butene are not significantly different. However, at an electron energy of 27 eV, differences in the fragmentation patterns of the isomers are augmented and the specific isomers could be distinguished.[11]

The identification of the specific butane and butene isomers formed during *tert*-butanethiol desulfurization was essential for testing the general mechanism proposed for straight-chain thiols. The formation of isobutane is most direct from hydrogenolysis of the *tert*-butanethiolate intermediate, as rearrangement to the primary alkane is thermodynamically unfavorable. The formation of isobutene from the dehydrogenation of the *tert*-butanethiolate intermediate at the 2-carbon also agrees with our mechanism. Dehydrogenation at the 2-carbon had been previously proposed for the straight-chain thiols,[14,75,85] and these results gave supporting evidence to this premise.

The selective dehydrogenation at the 2-position suggests that C–S bond breaking precedes C–H bond breaking. The C–H bond at the 1-carbon is expected to be more readily cleaved than the 2-C–H bond in an intact thiolate since the electronegative sulfur is expected to decrease the homolytic bond strength for the C–H bond at the 1-position. Such selectivity has been demonstrated for various alkoxides on metal surfaces.[88–91] Formation of a hydrocarbon radical or cation via cleavage of the C–S bond, would remove the preference for dehydrogenation at the 1-carbon; dehydrogenation at the 2-carbon is the expected result.

6.2. Coadsorption Experiments on Mo(110)

In order to learn more about the relative importance of C–S and C–H bond breaking and making in thiol desulfurization, the competitive reactions of various thiols were studied on Mo(110). Since the concentration of surface adsorbates, such as adsorbed carbon, sulfur, oxygen, hydrogen, or hydrocarbon fragments, is known to have a dramatic effect on reaction kinetics,[64,67,92,93] it is imperative that coadsorption experiments be done to ensure that the reaction conditions are identical for the intermediates being compared.

6.2.i. Effect of Chain Length on Thiol Desulfurization Kinetics

The reactions of a coadsorbed mixture of the linear alkanethiols (C_2–C_5) were studied on Mo(110) in an effort to learn about the effect of chain length on thiol desulfurization kinetics. All of the thiolates produce the corresponding alkanes with similar line shapes and peak temperatures, confirming that all primary thiolates react with essentially the same kinetics on Mo(110).[94] Since the C–S bond strength is basically the same for all of the primary thiols studied, this suggests that the rate-limiting step in hydrocarbon formation from the thiolate is C–S bond cleavage and independent of chain length.

6.2.ii. Effect of C–S Bond Strength on Thiol Desulfurization Kinetics

The relative rates of ethanethiolate and *tert*-butanethiolate hydrogenolysis provide supporting evidence that there is a major component of C–S bond cleavage in the transition state leading to alkanes. Isobutane is formed more rapidly from *tert*-butanethiolate hydrogenolysis than ethane is from ethanethiolate hydrogenolysis.[11] Both *tert*-butanethiolate and ethanethiolate have been identified by X-ray photoelectron and high-resolution electron energy loss spectroscopy.[11,14]

Our mechanism was further tested by studying the reactions of 2-propene-1-thiol on Mo(110). According to the proposed mechanism, propene formation from 2-propene-1-thiol should occur with the fastest kinetics of all thiols studied. Indeed, propene is formed most rapidly, at temperatures below 120 K, during the reaction 2-propene-1-thiol on Mo(110).[87] Dosing 2-propene-1-thiol on Mo(110) at 120 K leads to the immediate hydrogenolysis of the C–S bond to form adsorbed propene and atomic sulfur. Further heating of the surface, causes propene desorption from the surface.

6.3. Thiols on a Sulfided Mo(110) Surface

It is important to understand the effect of sulfur on the mechanism and kinetics for thiol desulfurization on Mo(110) since the working catalyst used in hydrodesulfurization consists of MoS_2-like particles and sulfur is deposited on the surface during the desulfurization of thiols. Only preliminary studies have been performed, but the study of desulfurization on sulfur overlayers will certainly be an expanding field. The reactions of benzenethiol on a sulfided Mo(110) surface were chosen for investigation as the reactions of benzenethiol on the clean Mo(110) surface were well understood, and the effect of adsorbed sulfur should be able to be delineated.

The reaction of benzenethiol on Mo(110) yields benzene via C–S bond hydrogenolysis of benzenethiolate with ~40% selectivity. Competing C–S and C–H bond scission produces adsorbed benzyne, which has been identified spectroscopically. The surface benzyne intermediate is stable up to 670 K, where it undergoes C–H and C–C bond scission to form adsorbed carbon and gaseous dihydrogen.

Benzenethiol on sulfided Mo(110) reacts with different kinetics than on the clean surface. Both C–S and C–H bond scission kinetics are slower on the sulfided surface, compared to the clean. The slower C–H scission kinetics are proposed to account for the higher selectivity for benzene formation on the sulfided surface, ~80%, since nonselective C–H bond scission is retarded by sulfur, allowing for more hydrogenolysis of the benzenethiolate.

6.4. Thiols on Other Surfaces

The reactions of methanethiol have been studied on metal surfaces other than Mo(110) due to its relative simplicity. Methanethiol forms methanethiolate, CH_3S^-, as a stable intermediate on Cu(100),[95] Cu(111),[96,97] Cu(410),[98] Ni(100),[96,99] Ni(110),[100] Ni(111),[101] Pt(111),[102] Fe(100),[103] W(211),[104] and Mo(110).[87] The exception is methanethiol on Au(111): the S–H bond

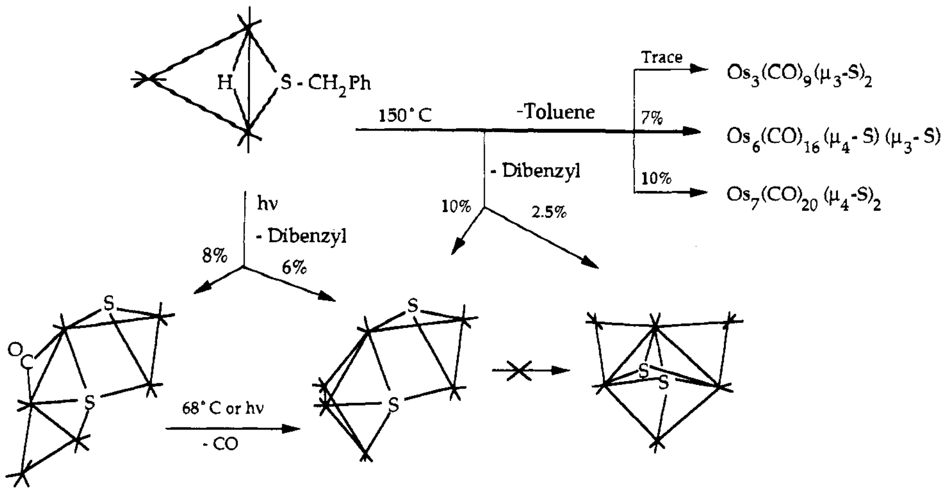


Figure 12. Proposed reaction scheme for toluenethiol with an osmium cluster (reprinted from ref 122; copyright 1983 American Chemical Society).

remains intact on this surface and molecular desorption is exclusively observed.[105]

The methanethiolate intermediate forms methane from C–S bond breaking and C–H bond formation on all of the surfaces investigated. Nonselective decomposition, which involves C–H bond breaking, is also observed. Indeed, on Pt(111), evidence for a dehydrogenated CH_2S^- intermediate was presented.[102] In methanethiol there is no stable gas-phase product of concomitant C–S and C–H bond breaking. Methylene radicals are expected to be trapped on the surface, if formed, and could ultimately lead to decomposition products. Ethane formation is also seen from the reaction of two methyl groups on Cu(100),[95] Ni(110),[100] Ni(100),[99] and Ni(111).[101]

The initial step proposed for methane formation from the methanethiolate intermediate is thought to be C–S bond breaking. In the case of Fe(100), C–S bond breaking to produce methyl radical is proposed to occur first and subsequent hydrogenation would afford methane. On the other hand, a one-step hydrogenolysis of the methanethiolate intermediate is proposed for Ni(110) and Mo(110).[87,100]

The thermodynamic driving force for C–S bond scission in thiol desulfurization on Mo(110) is proposed to be formation of the strong Mo–S bond. Weakening of the ν(C–S) mode by ~20–100 cm^{-1} in methanethiol has been seen previously on Fe(100),[103] Cu(100),[95] and Ni(110),[100] where methane was formed via C–S bond scission during the reaction. In these cases, a strong metal–S bond is also formed. An analogous weakening of the C–S bond occurs upon adsorption of *tert*-butanethiol on Mo(110). This weakening is proposed to facilitate the desulfurization of *tert*-butanethiol on Mo(110).

The reactions of methanethiol on single-crystal metal surfaces are different than the reactions of the oxygen analogue, methanol. On most metal surfaces, C–O bond retention, during methanol reaction, and carbon monoxide and dihydrogen formation are seen. One exception is Mo(110) which induces C–O bond cleavage and nonselective decomposition.[106,107] The propensity for C–S bond cleavage in methanethiol is proposed to be due to the relatively weaker C–S bond strength, ~80 kcal/mol, compared to the C–O strength of 91 kcal/mol bond in methanol.

The comparison in the reactivity of the methanethiol and methanol suggests that C–S bond cleavage plays an important role in determining the rate of reaction on other metal surfaces as well as Mo(110). This is in excellent agreement with the work done on Mo(110), where substitution of various alkyl substituents changed desulfurization kinetics dramatically.

The reactions of more complex thiols on metal surfaces have not been widely studied. Benzenethiol is proposed to form benzenethiolate on Cu(110)[108] and Cu(111).[109] Recently, several longer chain thiols have been studied on Cu(110) using ultraviolet photoelectron spectroscopy.[98] Again, formation of the corresponding thiolate is proposed.[98]

6.5. Comparison to Organometallic Complexes

6.5.i. C–S Bond Strength

The dependence of thiol desulfurization kinetics on C–S bond strength seen on Mo(110) is analogous to metal clusters. For example, benzylic thiols, which have the weakest C–S bonds, were desulfurized by $Co_2(CO)_8$,[110–113] $Mo(CO)_6$,[114] $Fe_3(CO)_{12}$,[113,115] $W(CO)_6$,[116–118] $HFe(CO)_4^-$,[119,120] and $Mn_2(CO)_{10}$,[121] all carbonyls of metals often used in hydrodesulfurization reactions. Toluenethiol is desulfurized in the $HOs_3(CO)_{10}(\mu\text{-}SCH_2C_6H_5)$ complex, during pyrolysis to form toluene and dibenzyl (Figure 12). A radical intermediate is proposed to account for dibenzyl formation, while direct elimination of toluene also occurs. Under photolytic conditions, C–S bond homolysis is the preferred route.[122] Similarly, the desulfurization of *tert*-butanethiol, a tertiary thiol, is seen in ruthenium[123] and niobium complexes.[124,125]

In contrast, the observed desulfurization of benzenethiolate in metal clusters is surprisingly different from that seen for metal surfaces. Benzenethiol has a relatively strong C–S bond and is expected to be difficult to desulfurize. However, desulfurization of benzenethiolate to form benzene has been seen in many cases. For example, desulfurization of benzenethiolate by a triosmium cluster leads to benzene formation from either thermolysis,[126,127] photolysis, or high CO pressure.[127] For the conditions of thermolysis and CO pressure, a metal-activated process is the preferred mechanism; while for photolysis, C–S bond homolysis is thought to be the driving mechanism.

Secondly, polynuclear binding was seen to be vital for thiol desulfurization, in analogy to what is believed to occur on metal surfaces. Desulfurization of benzenethiolate was also seen to occur in ruthenium complexes via pyrolytic or photolytic conditions.[79] Similar results were seen for the reaction in Ni or Pd compounds.[128]

Competing desulfurization of alkyl phenyl sulfides with $Os_3(CO)_{12}$ showed exclusive scission of the aryl C–S bonds.[129] This is in contrast to what is observed on surfaces, where desulfurization of alkanethiols occurred faster than for benzenethiol.

As seen for the cyclic sulfides, a tungsten complex, $WCl_2(PMePh_2)_4$, induced desulfurization of alkyl thiols.[130] Both ethanethiol and *tert*-butanethiol undergo desulfurization upon reaction to form the corresponding alkane and $W(S)Cl_2(PMePh_2)_3$. Desulfurization of thiols occurs much faster than deoxygenation of alcohols, consistent with the weaker bond strength of the thiols studied. In fact, no C–O bond cleavage was observed during reaction with phenol or *o*-cresol, alcohols with high C–O bond strengths. A one-step hydrogenolysis was also observed, again in good agreement with observed results for the surface.

6.5.ii. Importance of a Hydrogen Source

Surface hydrogen was shown to be very important in cyclic sulfide desulfurization. However, in the case of the thiol desulfurization on metal surfaces, formation of the surface thiolate intermediate via S–H bond scission produces a stoichiometric amount of hydrogen. As an example, the selectivity for hydrocarbon formation vs nonselective decomposition is much higher for the thiols compared to the corresponding cyclic sulfides. The selectivity for butane and butene formation was much higher for temperature-programmed reaction of 1-butanethiol (70%) than for tetrahydrothiophene (25%) on Mo(110). In contrast, coordination of thiols with metal clusters results most of the time with a thiolate ligand, without a hydride ligand.

Recently, characterized metal hydride thiolate complexes have been synthesized. In particular, intermolecular attack on an aryl C–S bond in the $Mo(H)(SC_6H_2R_3\text{-}2,4,6)_3(PR'Ph_2)$ complex, where R = methyl or isopropyl and R′ = methyl or ethyl produces $C_6H_3R_3\text{-}2,4,6$ and $[\{Mo(SC_6H_2R_3\text{-}2,4,6)(OMe)(PR'Ph_2)\}_2(\mu\text{-}S)_2]$ in a THF–MeOH solution.[131] Similarly, a tungsten hydride complex also led to C–S bond desulfurization.[132]

Another source of hydride has been the reactions of metal complexes with lithium aluminum[133-135] or tributyltin hydride.[136,137] Specifically, nickel lithium aluminum hydride complexes have been found to be ideal catalysts for desulfurization of sulfur-containing molecules.[133-135] As seen before for other systems, arylic and benzylic thiols underwent desulfurization more readily than aliphatic thiols. The mechanism proposed for thiol desulfurization in these cases has been intramolecular hydride transfer, analogous to the proposed surface mechanism.

6.6. Conclusions

As seen before for the reactions of thiophene and cyclic sulfides, there are many similarities between the desulfurization reactions of thiols on metal surfaces and in organometallic complexes. Firstly, the key reaction intermediate in all cases was the thiolate intermediate. On metal surfaces, S–H bond scission was seen in all cases where desulfurization occurred. Secondly, thiol desulfurization kinetics were seen to be driven by C–S bond strengths on both metal surfaces and in organometallic complexes. Thirdly, the presence of a hydrogen source was important in both cases. On metal surfaces, a stoichiometric amount of hydrogen was present due to S–H bond cleavage upon thiolate formation. Likewise, desulfurization of thiols was aided greatly by either the presence of a hydride source in the reaction mixture or a hydride ligand directly on the complex.

The ease of C–S bond scission in aryl thiolato organometallic complexes is in contrast to that seen on metal surfaces. On Mo(110), the aryl C–S bond is one of the hardest bonds to cleave. In fact, in comparison to alkyl C–S bonds, desulfurization kinetics are slower for the aryl C–S bond. In organometallic clusters, however, aryl C–S bonds were cleaved preferentially in alkyl phenyl sulfides. In fact, there are many instances of aryl C–S bond cleavage in the organometallic literature.

7. Outlook and Future Directions

Although there are many challenges left in determining the mechanism for hydrodesulfurization, much progress has been made. Importantly, new and exciting synthetic pathways to thiophenic and thiolate intermediates in organometallic complexes have opened up an exciting branch of chemistry. Further studies of these molecules can now be accomplished using both large scale and mixed metal clusters. In fact, desulfurization of thiols in mixed metal clusters has been studied and has proven very promising.[81,138-140]

Likewise, the systematic study of the reaction of different thiols on Mo(110), as well as studies on other surfaces has laid the groundwork for more exciting work. Great strides have been made in understanding basic principles of the thiol desulfurization on Mo(110). These initial studies allow for more detailed studies into the transition state of thiol desulfurization using molecules that are known to undergo rearrangements. Secondly, these initial studies will allow for a deeper understanding about the desulfurization of sulfur-containing molecules on sulfided and bimetallic/sulfided surfaces. The understanding of the desulfurization of the thiols on the clean Mo(110) surface makes delineation of the effect of the surface coadsorbates less difficult.

In conclusion, the outlook of the combined effort of model desulfurization studies on single-crystal metal surfaces and on organometallic clusters is very promising. The accumulation of basic knowledge of the model desulfurization studies on metal surfaces and in organometallic complexes will hopefully transfer into a more detailed understanding of the hydrodesulfurization mechanism under catalytic conditions. These approaches, working in tandem, should lead to more insight into the hydrodesulfurization mechanism.

8. Acknowledgments

This work was supported by a grant from the Department of Energy, Basic Energy Sciences, under

Grant No. DE-FG02-84-13289. We would also like to acknowledge Dr. Per Uvdal and Ms. Robin Pachtman for carefully proofreading this document. We also thank Profs. Angelici (Iowa State University), Jones (University of Rochester), Masel (University of Illinois), and Adams (University of South Carolina) who generously provided some of the figures and offered constructive criticism.

9. References and Notes

(1) Schuman, S. C.; Shalit, H. *Catal. Rev.* **1970**, *4*, 245.
(2) Topsoe, H.; Clausen, B. S. *Catal. Rev.-Sci. Eng.* **1984**, *26*, 395.
(3) Alstrup, I.; Chorkendorff, I.; Candia, R.; Clausen, B. S.; Topsoe, H. *J. Catal.* **1982**, *77*, 397.
(4) Chianelli, R. R.; Ruppert, A. F.; Behal, S. K.; Kear, B. H.; Wold, A.; Kershaw, R. *J. Catal.* **1985**, *92*, 56.
(5) Villa Garcia, M. A.; Lindner, J.; Sachdev, A.; Schwank, J. *J. Catal.* **1989**, *119*, 388.
(6) Prins, R.; de Beer, V. H. J.; Somorjai, G. A. *Catal. Rev.-Sci. Engl.* **1989**, *31*, 1.
(7) Angelici, R. J. *Acc. Chem. Res.* **1988**, *21*, 387.
(8) Oh, S. H.; Fisher, G. B.; Carpenter, J. E.; Goodman, D. W. *J. Catal.* **1986**, *100*, 360.
(9) Fisher, G. B.; Oh, S. H.; Carpenter, J. E.; et al. Mechanisms of the Carbon Monoxide Oxidation and Nitric Oxide Reduction Reactions Over Single Crystal and Supported Rhodium Catalysts: High Pressure Rates Explained Using Ultrahigh Vacuum Surface Science. In *Studies in Surface Science and Catalysis*; Crucq, A., Frennet, A., Eds.; Elsevier: Amsterdam, 1987; Vol. 30 (*Catalysis and Automotive Pollution Control*), p 215.
(10) Schloegl, R.; Schoonmaker, R. C.; Muhler, M.; Ertl, G. *Catal. Lett.* **1988**, *1*, 237.
(11) Wiegand, B. C.; Uvdal, P.; Friend, C. M. *J. Phys. Chem.* **1992**, *96*, 4527.
(12) Due to spin–orbit coupling in the S(2p) ionized final state, two peaks are associated with each sulfur state separated by $\sim$1.2 eV in a ratio of $\sim$1:2.
(13) Roberts, J. T.; Friend, C. M. *J. Chem. Phys.* **1988**, *88*, 7172.
(14) Roberts, J. T.; Friend, C. M. *J. Phys. Chem.* **1988**, *92*, 5205.
(15) Liu, A. C.; Friend, C. M. *J. Chem. Phys.* **1988**, *89*, 4396.
(16) Saillard, J.-Y.; Hoffmann, R. *J. Am. Chem. Soc.* **1984**, *106*, 2006.
(17) Thomas, M. G.; Pretzer, W. R.; Beier, B. F.; Hirsekorn, F. J.; Muetterties, E. L. *J. Am. Chem. Soc.* **1977**, *99*, 743.
(18) Grassian, V. H.; Muetterties, E. L. *J. Phys. Chem.* **1986**, *90*, 5900.
(19) Muetterties, E. L. *Isr. J. Chem.* **1980**, *20*, 84.
(20) Friend, C. M. *Surface Chemistry*; Madix, R. J., ed.; Springer-Verlag: New York, submitted for publication.
(21) Angelici, R. J. *Coord. Chem. Rev.* **1990**, *105*, 61.
(22) Kraus, J.; Zdrazil, M. *React. Kinet. Catal. Lett.* **1977**, *6*, 45.
(23) Lipsch, J. M. J. G.; Schuit, G. C. A. *J. Catal.* **1969**, *15*, 179.
(24) Kolboe, S. *Can. J. Chem.* **1969**, *47*, 352.
(25) Chen, J.; Daniels, L. M.; Angelici, R. J. *J. Am. Chem. Soc.* **1991**, *113*, 2544.
(26) Draganjac, M.; Ruffing, C. J.; Rauchfuss, T. B. *Organometallics* **1985**, *4*, 1909.
(27) Choi, M. G.; Angelici, R. J. *Organometallics* **1991**, *10*, 2436.
(28) Choi, M. G.; Robertson, M. J.; Angelici, R. J. *J. Am. Chem. Soc.* **1991**, *113*, 4005.
(29) Ogilvy, A. E.; Skaugset, A. E.; Rauchfuss, T. B. *Organometallics* **1989**, *8*, 2739.
(30) Chen, J.; Angelici, R. J. *Organometallics* **1989**, *8*, 2277.
(31) Chen, J.; Angelici, R. J. *Organometallics* **1990**, *9*, 849.
(32) Skaugset, A. E.; Rauchfuss, T. B.; Stern, C. L. *J. Am. Chem. Soc.* **1990**, *112*, 2432.
(33) Sanchez-Delgado, R. A.; Marquez-Silva, R. L.; Puga, J.; Tiripicchio, A.; Tiripicchio Camellini, M. *J. Organometal. Chem.* **1986**, *316*, C35.
(34) Lockemeyer, J. R.; Rauchfuss, T. B.; Rheingold, A. L.; Wilson, S. R. *J. Am. Chem. Soc.* **1989**, *111*, 8828.
(35) Ganja, E. A.; Rauchfuss, T. B.; Stern, C. L. *Organometallics* **1991**, *10*, 270.
(36) Huckett, S. C.; Miller, L. L.; Jacobson, R. A.; Angelici, R. J. *Organometallics* **1988**, *7*, 686.
(37) Sauer, N. N.; Angelici, R. J. *Organometallics* **1987**, *6*, 1146.
(38) Spies, G. H.; Angelici, R. J. *Organometallics* **1987**, *6*, 1897.
(39) Hachgenei, J. W.; Angelici, R. J. *Organometallics* **1989**, *8*, 14.
(40) Hachgenei, J. W.; Angelici, R. J. *J. Organomet. Chem.* **1988**, *355*, 359.
(41) Huckett, S. C.; Sauer, N. N.; Angelici, R. J. *Organometallics* **1987**, *6*, 591.
(42) Lesch, D. A.; Richardson, J. W., Jr.; Jacobson, R. A.; Angelici, R. J. *J. Am. Chem. Soc.* **1984**, *106*, 2901.
(43) Chen, J.; Daniels, L. M.; Angelici, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 199.
(44) Choi, M. G.; Angelici, R. J. *J. Am. Chem. Soc.* **1989**, *111*, 8753.
(45) Chen, J.; Angelici, R. J. *Organometallics* **1990**, *9*, 879.
(46) Cordone, R.; Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1989**, *111*, 5969.
(47) Ruette, F.; Valencia, N.; Sanchez-Delgado, R. *J. Am. Chem. Soc.* **1989**, *111*, 40.
(48) Jones, W. D.; Dong, L. *J. Am. Chem. Soc.* **1991**, *113*, 559.
(49) Ogilvy, A. E.; Draganjac, M.; Rauchfuss, T. B.; Wilson, S. R. *Organometallics* **1988**, *7*, 1171.
(50) Gentle, T. M. *Energy Res. Abstr.* **1984**, *9*, 28229 (Abstract).
(51) Stohr, J.; Gland, J. L.; Kollin, E. B.; et al. *Phys. Rev. Lett.* **1984**, *53*, 2161.
(52) Lang, J. F.; Masel, R. I. *Surf. Sci.* **1987**, *183*, 44.
(53) Netzer, F. P.; Bertel, E.; Goldmann, A. *Surf. Sci.* **1988**, *201*, 257.
(54) Schoofs, G. R.; Preston, R. E.; Benziger, J. B. *Langmuir* **1985**, *1*, 313.
(55) Preston, R. E.; Benziger, J. B. *J. Phys. Chem.* **1985**, *89*, 5010.
(56) Kelly, D. G.; Odriozola, J. A.; Somorjai, G. A. *J. Phys. Chem.* **1987**, *91*, 5695.
(57) Zaera, F.; Kollin, E. B.; Gland, J. L. *Surf. Sci.* **1987**, *184*, 75.
(58) Roberts, J. T.; Friend, C. M. *Surf. Sci.* **1987**, *186*, 201.
(59) Cocco, R. A.; Tatarchuk, B. J. *Surf. Sci.* **1989**, *218*, 127.
(60) Zaera, F.; Kollin, E. B.; Gland, J. L. *Langmuir* **1987**, *3*, 555.
(61) Sexton, B. A. *Surf. Sci.* **1985**, *163*, 99.
(62) Richardson, N. V.; Campuzano, J. C. *Vacuum* **1981**, *31*, 449.
(63) Liu, A. C.; Friend, C. M. *J. Am. Chem. Soc.* **1991**, *113*, 820.
(64) Xu, H.; Friend, C. M. Manuscript in preparation.
(65) Xu, X.; Friend, C. M. Unpublished results.
(66) Spies, G. H.; Angelici, R. J. *Organometallics* **1987**, *6*, 1897.
(67) Wiegand, B. C.; Friend, C. M.; Roberts, J. T. *Langmuir* **1989**, *5*, 1292.
(68) Calhorda, M.; Hoffmann, R.; Friend, C. M. *J. Am. Chem. Soc.* **1990**, *112*, 50.
(69) Thomas, T. M.; Grimm, F. A.; Carlson, T. A.; Agron, P. A. *J. Electron Spectrosc. Relat. Phenom.* **1982**, *25*, 159.
(70) Tibbetts, G. G.; Burkstrand, J. M.; Tracy, J. C. *Phys. Rev. B* **1977**, *15*, 3652.
(71) Adams, R. D.; Pompeo, M. P. *Organometallics* **1990**, *9*, 2651.
(72) Adams, R. D.; Pompeo, M. P. *Organometallics* **1990**, *9*, 1718.
(73) Adams, R. D.; Belinski, J. A.; Pompeo, M. P. *Organometallics* **1991**, *10*, 2539.
(74) Boorman, P. M.; Chivers, T.; Mahadev, K. N. *Can. J. Chem.* **1977**, *55*, 869.
(75) Roberts, J. T.; Friend, C. M. *J. Am. Chem. Soc.* **1986**, *108*, 7204.
(76) King, R. B. *Inorg. Chem.* **1962**, *2*, 326.
(77) Beck, W.; Danzer, W.; Thiel, G. *Angew. Chem.* **1973**, *85*, 625.
(78) Calet, S.; Alper, H. *Tetrahedron Lett.* **1986**, *27*, 3573.
(79) Adams, R. D.; Babin, J. E.; Tasi, M. *Inorg. Chem.* **1986**, *25*, 4514.
(80) Adams, R. D.; Babin, J. E. *Inorg. Chem.* **1986**, *25*, 3418.
(81) Kovacs, J. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 1131.
(82) Adams, R. D.; Pompeo, M. P. *J. Am. Chem. Soc.* **1991**, *113*, 1619.
(83) Adams, R. D.; Chen, G.; Sun, S.; Wolfe, T. A. *J. Am. Chem. Soc.* **1990**, *112*, 868.
(84) Gentle, T. M.; Grassian, V. H.; Klarup, D. G.; Muetterties, E. L. *J. Am. Chem. Soc.* **1983**, *105*, 6766.
(85) Roberts, J. T.; Friend, C. M. *J. Am. Chem. Soc.* **1987**, *109*, 3872.
(86) Roberts, J. T.; Friend, C. M. *Surf. Sci.* **1988**, *198*, L321.
(87) Wiegand, B. C.; Uvdal, P.; Friend, C. M. Manuscript in preparation.
(88) Brainard, R. L.; Madix, R. J. *Surf. Sci.* **1989**, *214*, 396.
(89) Bowker, M.; Madix, R. J. *Surf. Sci.* **1982**, *116*, 549.
(90) Davis, J. L.; Barteau, M. A. *Surf. Sci.* **1987**, *187*, 387.
(91) Brainard, R. L.; Madix, R. J. *J. Am. Chem. Soc.* **1989**, *111*, 3826.
(92) Wiegand, B. C.; Friend, C. M. Manuscript in preparation.
(93) Serafin, J. G.; Friend, C. M. *J. Am. Chem. Soc.* **1989**, *111*, 4233.
(94) Roberts, J. T.; Friend, C. M. *J. Am. Chem. Soc.* **1987**, *109*, 4423.
(95) Sexton, B. A.; Nyberg, G. L. *Surf. Sci.* **1986**, *165*, 251.
(96) Bao, S.; McConville, C. F.; Woodruff, D. P. *Surf. Sci.* **1987**, *187*, 133.
(97) Seymour, D. L.; Bao, S.; McConville, C. F.; Crapper, M. D.; Woodruff, D. P.; Jones, R. G. *Surf. Sci.* **1987**, *189/190*, 529.
(98) Anderson, S. E.; Nyberg, G. L. *J. Electron Spectrosc. Relat. Phenom.* **1990**, *52*, 735.
(99) Castro, M. E.; Ahkter, S.; Golchet, A.; White, J. M.; Sahin, T. *Langmuir* **1991**, *7*, 126.
(100) Huntley, D. R. *J. Phys. Chem.* **1989**, *93*, 6156.
(101) Castro, M. E.; White, J. M. Manuscript in preparation.

(102) Zhu, X.-Y.; Castro, M. E.; Akhter, S.; White, J. M.; Houston, J. E. *Surf. Sci.* **1988**, *207*, 1.

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

(104) Benziger, J. B.; Preston, R. E. *J. Phys. Chem.* **1985**, *89*, 5002.

(105) Nuzzo, R. G.; Zegarski, B. R.; Dubois, L. H. *J. Am. Chem. Soc.* **1987**, *109*, 733.

(106) Serafin, J. G.; Friend, C. M. *Surf. Sci.* **1989**, *209*, L163.

(107) Serafin, J. G.; Friend, C. M. *J. Am. Chem. Soc.* **1989**, *111*, 8967.

(108) Agron, P. A.; Carlson, T. A.; Dress, W. B.; Nyberg, G. L. *J. Electron Spectrosc. Relat. Phenom.* **1987**, *42*, 313.

(109) Agron, P. A.; Carlson, T. A. *J. Vac. Sci. Technol.* **1982**, *20*, 815.

(110) Shim, S. C.; Antebi, S.; Alper, H. *Tetrahedron Lett.* **1985**, *26*, 1935.

(111) Shim, S. C.; Alper, H. *J. Org. Chem.* **1985**, *50*, 147.

(112) Antebi, S.; Alper, H. *Tetrahedron Lett.* **1985**, *26*, 2609.

(113) Alper, H.; Sibtain, F.; Heveling, J. *Tetrahedron Lett.* **1983**, *24*, 5329.

(114) Luh, T. Y.; Wong, C. S. *J. Org. Chem.* **1985**, *50*, 5413.

(115) Alper, H.; Sibtain, F. *J. Organomet. Chem.* **1985**, *285*, 225.

(116) Ng, C. T.; Wang, X.; Luh, T. Y. *J. Org. Chem.* **1988**, *53*, 2536.

(117) Yeung, L. L.; Yip, Y. C.; Luh, T. Y. *J. Chem. Soc., Chem. Commun.* **1987**, *13*, 981.

(118) Yeung, L. L.; Yip, Y. C.; Luh, T. Y. *J. Org. Chem.* **1990**, *55*, 1874.

(119) Alper, H. *J. Org. Chem.* **1975**, *40*, 2694.

(120) Alper, H.; Paik, H.-N. *J. Org. Chem.* **1977**, *42*, 3522.

(121) Alper, H. *J. Organometal. Chem.* **1974**, *73*, 359.

(122) Adams, R. D.; Horvath, I. T.; Mathur, P.; Segmueller, B. E. *Organometallics* **1983**, *2*, 996.

(123) Bruce, M. I.; Shawkataly, O. b.; Snow, M. R.; Tiekink, E. R. T. *Aust. J. Chem.* **1986**, *39*, 1109.

(124) Seela, J. L.; Huffman, J. C.; Christou, G. *Polyhedron* **1989**, *8*, 1797.

(125) Skripkin, Y. V.; Eremenko, I. L.; Pasynskii, A. A.; Struchkov, Y. T.; Shklover, V. E. *J. Organomet. Chem.* **1984**, *267*, 285.

(126) Adams, R. D.; Yang, L. W. *J. Am. Chem. Soc.* **1982**, *104*, 4115.

(127) Adams, R. D.; Horvath, I. T.; Segmueller, B. E.; Yang, L. W. *Organometallics* **1983**, *2*, 1301.

(128) Osakada, K.; Hayashi, H.; Maeda, M.; Yamamoto, T.; Yamamoto, A. *Chem. Lett.* **1986**, 597.

(129) Adams, R. D.; Katahira, D. A.; Yang, L. W. *Organometallics* **1982**, *1*, 235.

(130) Jang, S.; Atagi, L. M.; Mayer, J. M. *J. Am. Chem. Soc.* **1990**, *112*, 6413.

(131) Burrow, T. E.; Hills, A.; Hughes, D. L.; et al. *J. Chem. Soc., Chem. Commun.* **1990**, *24*, 1757.

(132) Boorman, P. M.; Moynihan, K. J.; Patel, V. D.; Richardson, J. F. *Inorg. Chem.* **1985**, *24*, 2989.

(133) Ho, N. F.; Mak, T. C. W.; Luh, T. Y. *J. Chem. Soc., Dalton Trans.* **1990**, *12*, 3591.

(134) Ho, K. M.; Lam, C. H.; Luh, T. Y. *J. Org. Chem.* **1989**, *54*, 4474.

(135) Ho, N. F.; Mak, T. C. W.; Luh, T. Y. *J. Organomet. Chem.* **1986**, *317*, C28.

(136) Schmidt, K.; O'Neal, S.; Chan, T. C.; et al. *Tetrahedron Lett.* **1989**, *30*, 7301.

(137) Gutierrez, C. G.; Summerhays, L. R. *J. Org. Chem.* **1984**, *49*, 5206.

(138) Hitchcock, P. B.; Lappert, M. F.; McGeary, M. J. *Organometallics* **1990**, *9*, 2645.

(139) Hitchcock, P. B.; Lappert, M. F.; McGeary, M. J. *J. Am. Chem. Soc.* **1990**, *112*, 5658.

(140) Boorman, P. M.; Fait, J. F.; Freeman, G. K. W. *Polyhedron* **1989**, *8*, 1762.