Heterogeneous Catalysis of the Hydrodesulfurization of Thiophenes in Petroleum: An Organometallic Perspective of the Mechanism

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Summary

Despite the large-scale commercial application of heterogeneous catalytic hydrodesulfurization (HDS) to the desulfurization of organosulfur compounds in petroleum, very little is known of the mechanisms likely to be involved in this process. Summarized in this Account are possible mechanisms for the HDS of thiophene (T) and benzo[b]thiophene (BT), which are based on studies of organometallic complexes containing these organosulfur compounds. It is proposed that the HDS of thiophene begins by π, i.e., η^5, adsorption of the thiophene at a metal site. This is supported by the very similar patterns for deuterium exchange in thiophene passed with D_2 over an HDS catalyst and in the η^5-thiophene ligand in (η^5-thiophene)RuCp$^+$. Not only is η^5-thiophene activated to deuterium exchange, but it is also susceptible to reactions with hydrides, presumably including surface metal hydrides, to give either direct cleavage of a thiophene C–S bond (observed on Ru) or formation of an allyl sulfide complex (observed on Mn). This latter intermediate is protonated to give adsorbed 2,3-dihydrothiophene, which can isomerize to 2,5-dihydrothiophene. The actual desulfurization step involves elimination of butadiene from 2,5-dihydrothiophene, leaving sulfur on the catalyst

surface. Most of the transformations in this mechanism have been demonstrated to occur on transition-metal complexes and/or HDS catalysts. Mechanisms for benzothiophene HDS are not as well developed, but reasonable steps, based on reactions of their organometallic complexes, are discussed.

Hydrodesulfurization (HDS) Process

Hydrodesulfurization (HDS) is the commercial process (eq 1)[1] whereby sulfur is removed from organosulfur compounds in petroleum-based feedstocks by treatment with H_2 at roughly 400 °C over a Co- or Ni-promoted Mo or W catalyst supported on Al_2O_3.[2]

$$C_xH_yS + 2H_2 \xrightarrow{\text{catalyst}} C_xH_{y+2} + H_2S \qquad (1)$$
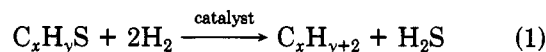
Because of the sheer volume (24 million barrels of petroleum per day worldwide in 1981)[3] of this process, it has been considered the most important chemical reaction presently practiced. There are several reasons for desulfurizing oil stocks: to prevent poisoning of sulfur-sensitive precious metal catalysts used in subsequent re-forming reactions, to remove the odor, and to reduce atmospheric pollution by sulfur oxides produced during the combustion of petroleum-based fuels.

Although petroleum feedstocks contain an incredibly complex mixture[4–6] of mercaptans, dialkyl and diaryl

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sulfides, and thiophenes, it is the thiophenes that are the most difficult to desulfurize and, for that reason, have been the focus of most HDS studies:

thiophene (T)   benzo[b]thiophene (BT)
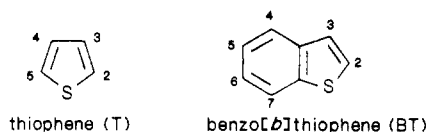
The HDS of thiophene itself (eq 2) gives H_2S and a mixture of C_4 hydrocarbons, the relative amounts depending on the catalyst and reaction conditions.

$$C_4H_4S + xH_2 \xrightarrow{\text{catalyst}}$$
$$\text{butadiene, } n\text{-butenes, } n\text{-butane} + H_2S \quad (2)$$
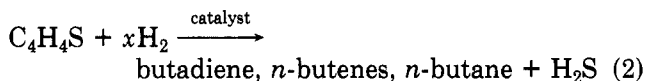
Despite the commercial importance of HDS, the mechanism(s) of even the simplest HDS reaction such as the process in eq 2 is (are) not known. Although progress has been made in characterizing the Mo/Al_2O_3 and $Co-Mo/Al_2O_3$ catalyst surfaces, the mode(s) of thiophene adsorption and reaction is (are) still not established. Our approach to understanding the mechanism(s) of thiophene HDS (eq 2) has been to prepare transition-metal complexes of thiophenes, examine their preferred modes of bonding and reactivity, and use the results to formulate a detailed mechanism that explains the observed reactivity of thiophenes on HDS catalysts.

Thiophene Adsorption Modes

Although $Co-Mo/Al_2O_3$ is the most-studied HDS catalyst because of its commercial relevance, many transition metals and/or their sulfides catalyze the HDS of thiophenes,[2,7,8] with Ru, Os, Rh, and Ir being among the most active. The lower cost of Mo makes it the industrial choice despite its lower activity.

Of the thiophene adsorption modes that have been proposed, the most commonly cited are the following

S – bound η^2 η^5
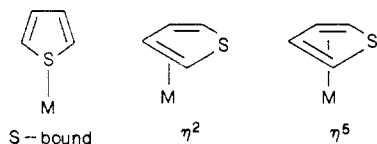
which represent S-bonding to a metal site, π-binding of two carbons (η^2), and π-binding of all five atoms (η^5) in the thiophene ring to a metal. The only infrared spectroscopic study[9] of thiophene adsorbed on MoS_2 and sulfided $Co-Mo/Al_2O_3$ gave results that were interpreted to indicate the presence of three forms: S-bound, η^2, and an η^4-form in which the four carbons were π-bonded to the surface. Several studies of thiophene on single-crystal surfaces have also been reported: on clean Ni(100),[10] Pt(111),[11] Cu(100),[12] and Cu(111)[13] and on clean and sulfided Mo(100),[14,15] Mo-

(110),[16] W(211),[17] Ni(111),[18] and Re(0001).[19] The results indicate that, depending on the metal, thiophene surface coverage, and temperature, the thiophene may be S-bonded perpendicular to the surface, S-bonded but tilted at an angle of ~40° with respect to the surface, or η^5-bonded parallel to the surface.

In transition-metal complexes, thiophene (T) is known to coordinate via the S atom or via all five atoms in the η^5 mode. Only four S-bound complexes have been isolated: $Ru(NH_3)_5(T)^{2+}$,[20] $CpFe(CO)_2(T)^+$,[21] (Cp = η^5-C_5H_5), $CpFe(NCMe)_2(2,5-Me_2T)^+$,[22] and $W-(CO)_3(PCy_3)_2(T)$.[23] In all cases, the thiophene is very easily displaced by weak ligands. The weakly coordinating nature of the S atom in thiophene is also illustrated by the many complexes where thiophene is part of a multidentate ligand yet either does not coordinate or interacts very weakly with the transition metal.[24] A well-characterized example of weakly coordinated thiophene in a chelate ligand is $(C_5H_4CH_2C_4H_3S)Ru-(PPh_3)_2^+$,[25] whose X-ray-determined structure reveals
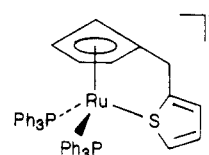
a pyramidal geometry around the sulfur such that the Ru–S vector forms a 126° angle with the vector from S to the C3–C4 bisector of the thiophene ring. A similar pyramidal geometry was found[26] at the sulfur in the thiaporphyrin complex $Cu(thiaporphyrin)(CO_3H)$, in which a thiophene replaces a pyrrole unit in the normal porphyrin ligand. Thus, there appears to be a strong tendency for the sulfur in S-bound thiophene ligands to move toward sp^3 hybridization. Previously, it had generally been assumed that the metal would lie in the plane of the thiophene, but now it is clear that this assumption is incorrect. The bent bonding readily accounts for the tilted thiophene bonding to single-crystal surfaces of Pt(111)[11] and Cu(100).[12]

Because of the weakly coordinating nature of S-bound thiophene, the only reported reaction of these complexes is displacement of the thiophene ligand from the metal. It seemed to us that η^5-thiophene would coordinate more strongly to the metal and possibly activate it in ways that may account for the reactivity of thiophene on HDS catalysts. There are several known η^5 complexes: $(\eta\text{-T})Cr(CO)_3$,[27] $(\eta\text{-T})Mn(CO)_3^+$,[24,28] ($\eta$-

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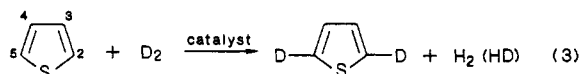
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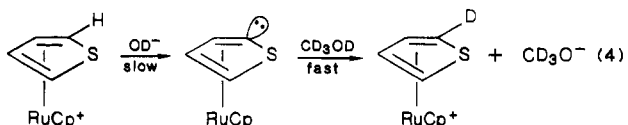
T)FeCp$^+$,[29] (η-T)RuCp$^+$,[30,31] (η-T)M(PPh$_3$)$_2^+$ (M = Rh, Ir),[32] and Cp*M(η-T)$^{2+}$ (M = Rh, Ir; Cp* = η-C$_5$Me$_5$).[33] X-ray structure determinations of (η-T)Cr(CO)$_3$[34] and (η-T)Rh(PPh$_3$)$_2^+$ [32] show that all five atoms of the thiophene ring are coordinated to the metal. The generally high stability of these η^5-thiophene complexes suggests that this may be the preferred mode of bonding to transition metals on catalyst surfaces. We thus sought to study the complexes with a view toward explaining the reactivity of thiophene on HDS catalysts.

Deuterium Exchange of Thiophene on HDS Catalysts

A reaction that generally occurs more rapidly on HDS catalysts than HDS itself is the exchange of protons in thiophene with deuterium (eq 3). These exchange

$$\underset{5\ \underset{S}{}\ 2}{\overset{4\ \underline{}\ 3}{\diagup\!\diagdown}} + D_2 \xrightarrow{catalyst} D\!-\!\diagup\!\!\diagdown_S\!-\!D + H_2 \text{ (HD)} \quad (3)$$

reactions have been studied at relatively mild temperatures (160–300 °C), where little HDS of thiophene occurs, over MoS$_2$,[35,36] Mo/Al$_2$O$_3$,[37] Co–Mo/Al$_2$O$_3$,[37] and Chevrel phase M$_x$Mo$_6$S$_8$[38] catalysts. In all cases, preferential exchange occurs in the 2- and 5-positions, which has been explained[36,37] in terms of thiophene adsorption via the S atom; this places the 2- and 5-hydrogens near the catalyst surface where exchange might occur. In view of the preference for η^5-thiophene bonding in transition-metal complexes and the possibility that it would be involved during deuterium exchange, we examined[39] the relative exchange rates of thiophene protons in (η-T)RuCp$^+$ with deuteriated methanol (CD$_3$O-D) in the presence of base (OD$^-$). The rates of exchange of the 2,5-hydrogens in the thiophene are too fast to measure even at very low concentrations of the OD$^-$ catalyst. The 3,4-hydrogens exchange at least 150 times slower, following a rate law that is first order each in the (η-T)RuCp$^+$ and OD$^-$ concentrations. A mechanism involving rate-determining deprotonation followed by rapid deuteriation was proposed for exchange at both the 2,5- and 3,4-hydrogens in the complex (eq 4). The

$$\underset{RuCp^+}{\diagup\!\!\diagdown_S}\overset{H}{} \xrightarrow[\text{slow}]{OD^-} \underset{RuCp}{\diagup\!\!\diagdown_S} \xrightarrow[\text{fast}]{CD_3OD} \underset{RuCp^+}{\diagup\!\!\diagdown_S}\overset{D}{} + CD_3O^- \quad (4)$$

Ru presumably enhances the exchange as compared with free thiophene, which does not exchange under these conditions, by withdrawing electron density from

Figure 1. Percent deuteration, given in parentheses, in the various positions of the thiophenes over Mo/Al$_2$O$_3$ at 200 °C[37] and rate constants 10^3k (M^{-1} s^{-1}), given in square brackets, for deuterium exchange in (η-Me$_x$C$_4$H$_{4-x}$S)RuCp$^+$ in OD$^-$/CD$_3$OD at 23 °C.[39]

the thiophene ring, thus making all of the protons more easily abstracted by OD$^-$. The Ru does not change the relative order of acidity of the protons from that in free thiophene, since the 2,5-protons of thiophene are also preferentially removed by very strong bases such as lithium alkyls.[40]

The deuterium exchange of several methyl-substituted thiophene complexes (η-Me$_x$C$_4$H$_{4-x}$S)RuCp$^+$ was also studied;[39] in all cases, the 2,5-protons exchange much more rapidly than H$_{3,4}$; the CH$_3$ hydrogens were by far the slowest to exchange. The rate constants for these exchanges, together with the percentages of deuteriation[37] of the thiophenes by D$_2$ over Mo/Al$_2$O$_3$ at 200 °C, are shown in Figure 1. In both the Ru complexes and over the Mo/Al$_2$O$_3$ catalyst, the extent of exchange decreases in the order H$_{2,5}$ > H$_{3,4}$ > CH$_3$. Thus, the η^5-thiophene bonding mode reasonably accounts for the order of exchange over HDS catalysts.

It was further demonstrated that the 2,5-protons of (η-T)RuCp$^+$ adsorbed on deuteriated Al$_2$O$_3$(OD$_2$) undergo exchange with surface OD groups on the Al$_2$O$_3$.[30] These results suggest a mechanism for deuterium exchange on HDS catalysts that involves initial η^5-thiophene adsorption on a metal center, deprotonation by basic sites on the MoS$_2$ or Al$_2$O$_3$ support, and deuteriation by surface SD or OD groups.

One trend in the data in Figure 1 that warrants further comment is the extent of H$_{3,4}$ exchange with increasing methyl substitution. The rate of H$_{3,4}$ exchange in (η-Me$_x$C$_4$H$_{4-x}$S)RuCp$^+$ decreases in the order thiophene > 2-methylthiophene $\geq$ 2,5-dimethylthiophene. As expected, the electron-donating methyl groups decrease the acidity of H$_{3,4}$, thereby decreasing their rate of base-promoted deprotonation and therefore their rate of exchange. In contrast, over the Mo/Al$_2$O$_3$ catalyst, the extent of deuteriation decreases in the opposite order, with the most methyl-substituted thiophenes undergoing the greatest amount of deuteriation. This trend may be understood by considering both the adsorption and exchange steps (eq 5) on the catalyst. Since the exchange step, k, is likely (eq 4) to

$$\underset{}{\diagup\!\!\diagdown_{S(g)}} + M_{surface} \underset{\text{fast}}{\overset{K_{ads}}{\rightleftharpoons}} \underset{\underset{M_{surface}}{|}}{\diagup\!\!\diagdown_S} \xrightarrow[\text{slow}]{k} D \text{ exchange} \quad (5)$$
$$\text{or HDS}$$

be slower for the more methyl-substituted thiophenes, the increase in H$_{3,4}$ exchange with increasing methyl substitution could be understood only if K_{ads} increases substantially with increasing methyl substitution. That

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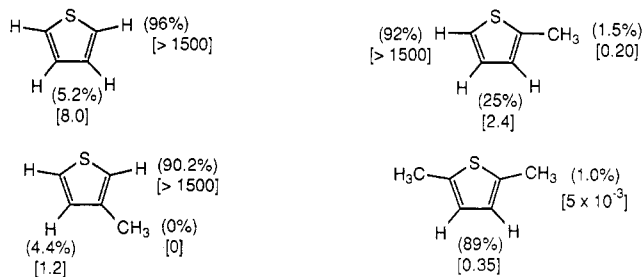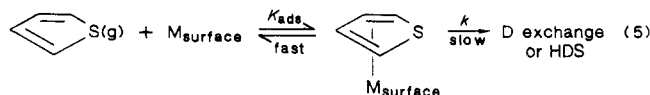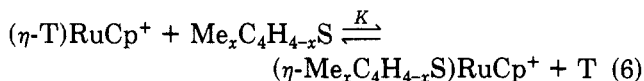(39) Sauer, N. N.; Angelici, R. J. *Organometallics* **1987**, *6*, 1146.

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this is likely to be the case is suggested by equilibrium constants for (η-thiophene)RuCp$^+$ exchange reactions (eq 6),[41] which decrease in the order 2,5-dimethyl-

$$(\eta\text{-T})RuCp^+ + Me_xC_4H_{4-x}S \overset{K}{\rightleftharpoons}$$
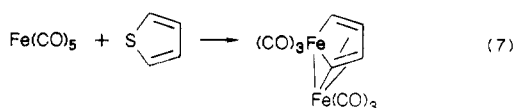$$(\eta\text{-}Me_xC_4H_{4-x}S)RuCp^+ + T \quad (6)$$

thiophene (32) > 2-methylthiophene (6) > thiophene (1.0); K values are in parentheses. These relatively large differences in equilibrium constants for reaction 6 suggest that the more methyl-substituted thiophenes will adsorb more to the catalyst surface, which is why $H_{3,4}$ exchange increases with increasing methyl substitution. These differences in K_{ads} presumably outweigh the opposite trend in rates (k) of exchange of the adsorbed thiophenes.

Mechanisms for the HDS of Thiophene

Several mechanisms for thiophene HDS have been proposed based on reactor studies.[42] However, it has not yet been established whether thiophene undergoes initial C–S bond cleavage to give butadiene that is rapidly hydrogenated to the observed mixture of C_4 products (eq 2) or the thiophene is initially hydrogenated to di- or tetrahydrothiophenes that subsequently yield the C_4 products. Thus, the proposed mechanisms involve either initial C–S cleavage[43,44] or partial hydrogenation.[45] All proposals involve either S-, η^5-, or η^2-binding of the thiophene to a metal site; this binding is proposed to activate the thiophene to participate in reactions that eventually lead to desulfurization. A major weakness of all the proposals is the lack of direct evidence for any type of thiophene activation by coordination to a metal. Moreover, one could easily imagine other modes of thiophene reaction that would constitute the basis for other mechanistic proposals. Thus, it seems useful to examine relatively simple reactions of thiophene in transition-metal complexes.

One of the first reactions of this type was that of $Fe(CO)_5$ with thiophene (eq 7);[46] recent studies[47] indi-

cate that the final ferrole product is formed from a thiaferrole intermediate, $Fe_2(C_4H_4S)(CO)_6$. The same ferrole product can be obtained from the reaction of vaporized Fe(g) atoms and thiophene in a CO atmosphere.[48] The ferrole reacts with H_2 to give butadiene and 1-butene.[49] Thus, one might consider the $Fe(CO)_5$ and Fe(g) systems as models for reactions occurring on HDS catalyst surfaces. Thiophene is also readily desulfurized by Ni(0) complexes[50] and on surfaces of single

crystals of metals, Mo(100),[14,15] Mo(110),[16] and Ni-(100).[10] All of these strongly reducing metals are likely to be more reactive than metals present in HDS catalysts. Thus, sulfided Mo(100),[15] while less active than Mo(100), is probably a better model for Mo-based HDS catalysts.

Our HDS model studies began by considering η^5-thiophene as a likely form for the adsorption and activation of thiophene. On the basis of the known[2,51] olefin hydrogenation activity of many HDS catalysts, it seemed likely that metal hydride species would be present on the catalyst surface as a result of dissociative adsorption of H_2. As rather primitive models for such species, we used $HFe(CO)_4^-$ and $HW(CO)_5^-$ and explored their reactions with the η^5-thiophene complex $(\eta\text{-T})Mn(CO)_3^+$. In CH_2Cl_2 at room temperature, both hydride complexes transfer H$^-$ to the 2-position of the thiophene, giving an η^4-C_4H_5S allyl sulfide complex, I (eq 8).[24] The reaction with $DFe(CO)_4^-$ showed that exo

$M(CO)_x = Fe(CO)_4$ or $W(CO)_5$
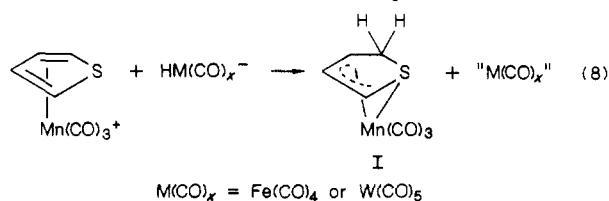
addition is somewhat favored, but attack at both sides of the thiophene is observed.[52] Since free thiophene did not react with $HFe(CO)_4^-$, the $Mn(CO)_3^+$ fragment is activating the thiophene to H$^-$ addition, presumably by withdrawing electron density and making the thiophene susceptible to attack by the hydride nucleophile. Similar additions to other π-hydrocarbon ligands have been studied in some detail.[53] If a reaction similar to (8) occurs on an HDS catalyst, it is an important step because it results in breaking the aromatic stabilization of the thiophene ring, and subsequent species such as the η^4-C_4H_5S allyl sulfide product are likely to be much more reactive. Thus, a reaction such as (8) could be rate determining for the overall HDS process.

The 2-methylthiophene complex $(\eta\text{-2-MeT})Mn(CO)_3^+$ undergoes H$^-$ attack by $HFe(CO)_4^-$ at the nonmethylated 5-position, but the 2,5-dimethylthiophene ligand in $(\eta\text{-2,5-Me}_2T)Mn(CO)_3^+$ does not undergo H$^-$ addition but more slowly forms other products.[52] Thus, it appears that Me groups in the 2,5-positions disfavor H$^-$ transfer as in eq 8, and one might expect the HDS rates of methyl-substituted thiophenes to decrease in the order T > 2-MeT > 2,5-Me$_2$T. The fact that the relative rates on Co–Mo/Al$_2$O$_3$ decrease in the opposite order, 2,5-Me$_2$T (2.0) > 2-MeT (1.5) > T (1.0),[54] suggests that the trend in HDS reactivity is controlled by the greater tendency of the more methyl-substituted thiophenes to adsorb to the catalyst surface, as was also proposed above (eq 5) to account for the trend in $H_{3,4}$

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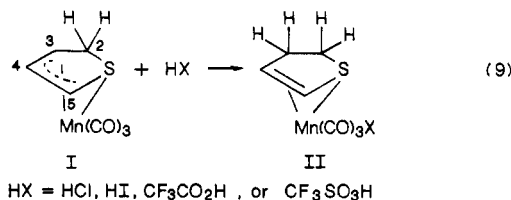(53) (a) Bush, R. C.; Angelici, R. J. *J. Am. Chem. Soc.* 1986, 108, 2735. (b) Kane-Maguire, L. A. P.; Honig, E. D.; Sweigart, D. A. *Chem. Rev.* 1984, 84, 525. (c) Kane-Maguire, L. A. P. In *Mechanisms of Inorganic and Organometallic Reactions*; Twigg, M. V., Ed.; Plenum: New York, 1986; p 359.
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exchange in methylthiophenes.

Assuming the first step in thiophene HDS to be H⁻ addition of the type in eq 8, how might the allyl sulfide intermediate (as in I in eq 8) react further? Of the species possibly present on Mo-based HDS catalysts, –SH groups have been identified on both MoS_2 and sulfided Mo/Al_2O_3.[55] It has been suggested that the –SH groups on MoS_2 are very strong protonic acids under HDS conditions, sufficiently acidic to protonate olefins to give carbonium ions.[56] Other studies,[57] however, show no evidence for such acidic groups. Of the transition-metal complexes with SH ligands, WS_2-$(SH)_2$ appears to be the most acidic, with a pK_a^1 of approximately –3,[58] comparable to H_2SO_4. The bridging –SH in $[Mo(NC_6H_4CH_3)(S_2P(OEt)_2)]_2(\mu\text{-}S)(\mu\text{-}SH)(\mu\text{-}O_2CCF_3)$ has an acidity that is comparable to those of Cl_2CHCO_2H and $ClCH_2CO_2H$.[59] But many other complexes with –SH ligands are weakly acidic.[60] Thus, there is a range of –SH ligand acidities in metal complexes, and it is at least plausible that strongly acidic –SH groups are present on MoS_2 catalysts under HDS conditions. We therefore, examined the reactions of I with several strong acids (eq 9);[24] the weaker acetic acid

$$\underset{\text{I}}{\underset{\text{Mn(CO)}_3}{\overset{\overset{\text{H H}}{\underset{4}{\overset{3}{<}}\underset{5}{\overset{2}{\underset{1}{\cdot}}}}S}{}}} + HX \longrightarrow \underset{\text{II}}{\underset{\text{Mn(CO)}_3X}{\overset{\overset{\text{H H}}{H\underset{}{\overset{}{|}}\underset{}{\overset{}{|}}H}}{S}}} \qquad (9)$$

$$HX = HCl, HI, CF_3CO_2H, \text{ or } CF_3SO_3H$$

did not react. The presence of the 2,3-dihydrothiophene (2,3-DHT) ligand in the product (II) was established for the X = Cl derivative. Presumably, protonation of I occurred at the 3-position because of the stability associated with the olefin and S groups being conjugated and coordinated to the metal. If protonation had occurred at the 5-position to give the thermodynamically more stable 2,5-DHT isomer,[61] coordination of both the sulfur and the olefin would have been sterically less favorable.

Reactions such as (8) and (9) involving successive H⁻ and H⁺ additions to an η^5-thiophene on an HDS catalyst would give 2,3-DHT as an intermediate. However, 2,3-DHT has not been detected as a product of thiophene HDS, which suggests that either it is not an intermediate or it is rapidly converted under HDS conditions to the observed products. That the latter is the case was demonstrated in a comparative study[62] of the HDS reactivity of thiophene and 2,3-DHT over Mo/Al_2O_3 and Re/Al_2O_3 catalysts at 300–400 °C in a continuous-flow fixed-bed microreactor. For example, at 400 °C over Mo/Al_2O_3, only 24.5% of the thiophene was converted to products, whereas all of the 2,3-DHT reacted. It is also interesting that the distributions of C_4 products (1-butene, *cis*- and *trans*-2-butene, and
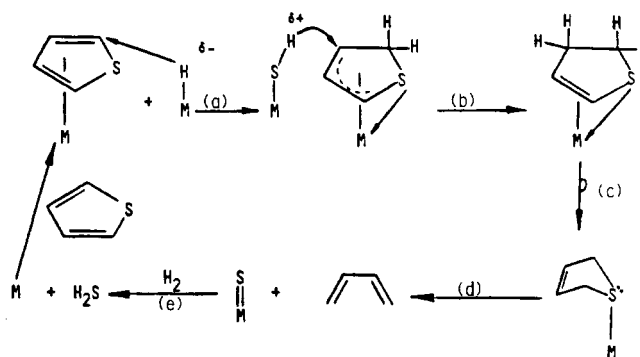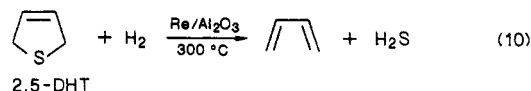

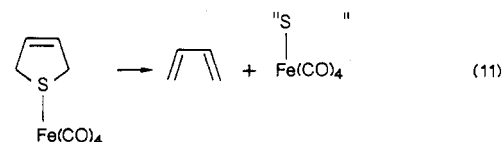**Figure 2.** Proposed mechanism for thiophene HDS.

butane) from the thiophene and 2,3-DHT reactions were very similar. Thus, the HDS of 2,3-DHT is much faster than that of thiophene, which is consistent with the possibility that 2,3-DHT is an intermediate.

If 2,3-DHT is an intermediate, one might ask how it undergoes desulfurization. A possible clue to this turned up in HDS reactor studies[62] of 2,3-DHT over Re/Al_2O_3 at a relatively low temperature (300 °C) where 39.6% of the 2,3-DHT goes unreacted. In addition to the usual C_4 products, there is a substantial amount (56.9% of the C_4 products) of butadiene as well as a significant amount (6.9%) of 2,5-DHT, both of which are not observed at 400 °C. Thus, it seemed possible that, at least under these conditions, the butadiene product could be generated by the elimination of S from 2,5-DHT (eq 10). That this does indeed occur was

$$\underset{\text{2,5-DHT}}{\overset{}{\underset{S}{\boxed{}}}} + H_2 \xrightarrow[\text{300 °C}]{Re/Al_2O_3} //\!\!\!\diagdown\diagdown + H_2S \qquad (10)$$

shown by a study of 2,5-DHT, which gives a C_4 product with 63.5% butadiene. Deuterium labeling studies[62] suggest that most of the butadiene is produced directly from 2,5-DHT; however, it is possible that some results from desulfurization of 2,3-DHT by another mechanism.

Since 2,5-DHT is known to coordinate via the sulfur in its $(CO)_5M(2,5\text{-DHT})$ complexes (M = Cr, W),[63] it seemed likely that 2,5-DHT would also bind to the Re on Re/Al_2O_3 and that this coordination would promote the loss of butadiene with the formation of a surface sulfide atom. That a metal is likely to promote such a reaction was demonstrated by the decomposition of $Fe(CO)_4(2,5\text{-DHT})$ (eq 11),[64] which occurs slowly even

$$\underset{\underset{Fe(CO)_4}{|}}{\overset{}{\underset{S}{\boxed{}}}} \longrightarrow //\!\!\!\diagdown\diagdown + \overset{\overset{\text{"S"}}{|}}{Fe(CO)_4} \qquad (11)$$

at room temperature in solution but rapidly when heated neat at 120 °C. The black solid residue obtained from the 120 °C reaction was presumably FeS. The decomposition in solution gave $\nu(CO)$ product bands suggesting the formation of iron–sulfur–carbonyl clusters, but they have not yet been identified. Nor has the mechanism of reaction 11 been established; while the

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butadiene may be eliminated in a single concerted step, it is not possible to exclude a more complex series of reactions.

On the basis of the above studies, we have proposed[64] the overall mechanism for thiophene HDS given in Figure 2. It involves initial η^5-adsorption of thiophene to a metal site, which activates the thiophene to H[^-] transfer from a nearby metal hydride (step a) to the 2-position of the thiophene, giving the allyl sulfide intermediate; this reaction is similar to that of $(\eta\text{-T})\text{Mn}(\text{CO})_3^+$ with metal hydrides (eq 8). Step b is analogous to reaction 9 in the sense that a strongly acidic proton, perhaps from an –SH group as suggested earlier, is transferred to the 3-position to give 2,3-DHT. The 2,3-DHT could be coordinated via both the sulfur and the olefin as shown in Figure 2 or it may be coordinated only through the sulfur as observed in its transition-metal complexes.[63,65] Steps a and b are equivalent to adding two hydrogen atoms, which is quite possible since HDS catalysts are also olefin hydrogenation catalysts. The isomerization of 2,3-DHT to the thermodynamically more stable 2,5-DHT in step c was observed on the $\text{Re}/\text{Al}_2\text{O}_3$ catalyst at 300 °C and presumably occurs by one of the traditional mechanisms for olefin isomerization on heterogeneous or homogeneous catalysts.[66] The actual desulfurization reaction is step d, which involves the elimination of butadiene promoted by the abstraction of a sulfur atom from the S-bound 2,5-DHT. This is a reaction that has been observed on $\text{Re}/\text{Al}_2\text{O}_3$ (eq 10) and in $\text{Fe}(\text{CO})_4(2,5\text{-DHT})$ (eq 11). The observed C_4 products, butenes and butane, are presumably formed by hydrogenation of butadiene, a reaction known to occur over HDS catalysts.[42] The final step, step e, converts a surface sulfide to H_2S by reaction with H_2.

Although the thiophene HDS mechanism in Figure 2 is the first to be based on reactions that are known to occur on metal centers and the overall mechanism is intuitively reasonable, it has not been proven (or disproven) to occur on any HDS catalyst. One approach to testing the mechanism is to compare the deuterium content of butadiene produced in the deuteriodesulfurization (DDS, using D_2 instead of H_2) of thiophene with that predicted by the mechanism in Figure 2. This mechanism predicts the addition of one deuterium in step a and another in step b. During the isomerization (step c) a third deuterium is added to the olefin adjacent to the sulfur, while a proton is removed from the 3-position. Since there are both a proton and a deuterium at the 3-position at this stage, it is possible that the deuterium would also transfer off the 2,3-DHT. This would probably occur only to a minor extent, since the deuterium isotope effect would greatly favor hydrogen transfer, as has been observed for H vs D exchange in the thiophene of $(\eta\text{-C}_4\text{H}_4\text{S})\text{RuCp}^+$ and $(\eta\text{-C}_4\text{D}_4\text{S})\text{RuCp}^+$ (eq 4);[39] the H exchange is more than 5.7 times faster than D exchange. Thus, after isomerization (step c), the 2,5-DHT would incorporate three deuterium atoms, and sulfur elimination in step d would give butadiene-d_3.

In deuteriodesulfurization (DDS) studies of thiophene over several HDS catalysts, the butadiene is observed

to contain 3.3–4.0 deuterium atoms, depending on the HDS catalyst used.[38] The somewhat higher observed D content than the three predicted by the mechanism in Figure 2 may easily be rationalized as coming from deuterium exchange into the thiophene as discussed earlier (eq 3) even before HDS occurs. The other source of additional deuterium in the butadiene may be exchange of the butadiene product itself with deuterium, which has been observed on MoS_2.[36,67] Thus, while the observed deuterium content of the butadiene is reasonably consistent with the predicted amount, DDS experiments that locate the deuterium atoms in the butadiene product for comparison with the predicted deuterium positions would be a more severe test of the mechanism.

Although Figure 2 offers a plausible mechanism for thiophene HDS, it is possible that there are other mechanisms depending on the catalyst and reaction conditions. Another such possibility turned up in reactions of hydrides with $(\eta\text{-T})\text{RuCp}^+$. Whereas the analogous reactions of $(\eta\text{-thiophene})\text{Mn}(\text{CO})_3^+$ with hydrides give an ally sulfide complex (eq 8), $(\eta\text{-thiophene})\text{RuCp}^+$ complexes react as in eq 12 to give
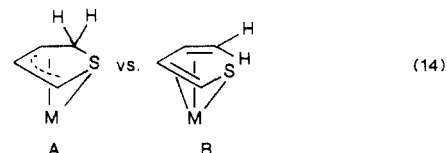

$$\text{XH}^- = \text{H}_2\text{Al}(\text{OCH}_2\text{CH}_2\text{OMe})_2^-,\ \text{AlH}_4^-,\ \text{or}\ \text{HBEt}_3^-$$
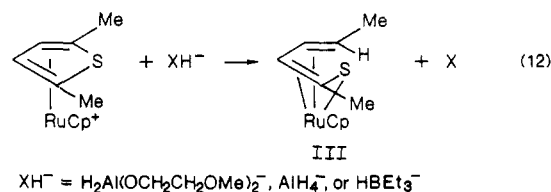
directly a product in which the C–S bond is cleaved, as established by an X-ray diffraction study.[68] Other nucleophiles (SMe^-, SEt^-, $\text{S}(i\text{-Pr})^-$, and $\text{CH}(\text{CO}_2\text{Me})_2^-$) also react with $(\eta\text{-thiophene})\text{RuCp}^+$ to give ring-opened products (eq 13).
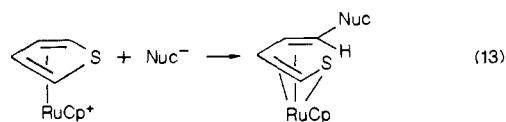
Reactions 12 and 13 with hydrides and the other nucleophiles probably proceed by different mechanisms since the nucleophile in the product of reaction 13 is syn whereas the hydride in reaction 12 is anti. Although no kinetic studies have been performed, it seems likely that the milder nucleophiles in eq 13 react by direct attack at the 2-carbon, whereas the hydrides in eq 12 react by another mechanism, perhaps involving an $(\eta\text{-thiophene})\text{RuCp}^\bullet$ radical intermediate analogous to $(\eta\text{-C}_4\text{Me}_4\text{S})\text{FeCp}^\bullet$, which has been detected by ESR at low temperature.[22b]

Although it is not clear why hydride adducts of $(\eta\text{-T})\text{Mn}(\text{CO})_3^+$ prefer the allyl sulfide closed-ring form (A in eq 14) whereas $(\eta\text{-T})\text{RuCp}^+$ adducts prefer the bu-

tadienethiolate form (B), it is tempting to link the high HDS activity of Ru catalysts[7] with the preference of Ru

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for the C–S cleaved form B and the low HDS activity of Mn to form A, which necessitates its following a higher energy HDS pathway, perhaps of the type in Figure 2.

Although a complete mechanism based on direct C–S bond cleavage (eq 12 and 13) cannot yet be formulated, compound III (eq 12) does react with H_2 (27 atm) at 110 °C to give *n*-hexane and an uncharacterized hexane-soluble $Cp_xRu_yS_z$ complex, indicating that the remaining C–S bond in III is easily cleaved. However, the mechanism of this cleavage has not been established.

Both thiophene HDS mechanisms, that in Figure 2 and the other based on reaction 12, assume η^5-adsorption which activates the thiophene to attack by surface hydride or possibly sulfide nucleophiles. Recent extended-Hückel MO calculations[69] also predict that η^5-thiophene would be the most active form of adsorbed thiophene as judged by the extent of C–S bond weakening; H addition to η^5-thiophene at the 2-position, rather than the 3-position, was also predicted to be more favorable and has been observed in the H⁻ addition reactions noted in eq 8, 12, and 13.

Because the allyl sulfide and butadienethiolate intermediates are likely to be much more reactive on HDS catalysts than thiophenes, the first two steps, thiophene adsorption (eq 5) and reaction with a surface nucleophile, will probably control the overall rate of thiophene HDS. Since thiophene is more likely to bond to metals in the lower oxidation states (0, +1, +2), as seen from the list of stable η^5-thiophene complexes cited in the introduction, the K_{ads} step (eq 5) is likely to be favored by metals in lower oxidation states. This may indeed be the reason why the Chevrel phase catalysts[70] $M_xMo_6S_8$, where M is Co, Ni, Fe, Cu, In, Ag, Sn, Pb, or Ho and the Mo is in a +2 to +2 2/3 oxidation state, are more active than MoS_2 in the +4 oxidation state. While the adsorption step is favored by low-oxidation-state metals, the nucleophilic attack step, k, is favored by higher oxidation states because the metal withdraws more electron density from the thiophene ring, which makes it more susceptible to nucleophilic addition, as has been demonstrated in numerous organometallic reactions.[53] Presumably an intermediate oxidation state would give the overall most active HDS catalyst.

Mechanisms for the HDS of Benzo[*b*]thiophene (BT)

Results of reactor studies[71,72] of benzo[*b*]thiophene (BT) HDS have been interpreted to mean that the initial steps involve hydrogenation to give 2,3-dihydrobenzo[*b*]thiophene. Further details of the adsorption mode and individual steps are still lacking. Possible adsorption modes include binding through the S atom or via the π-system of the benzene or thiophene rings or perhaps through both rings to two adjacent metal sites. In transition-metal chemistry, there are no examples of the two latter modes of coordination. There is only one example, $CpFe(CO)_2(BT)^{+,21b}$ of an S-bound BT complex; the BT is so weakly coordinated that it

is even displaced by nitromethane solvent. There is no evidence that the BT is activated to react.

There are now several examples of stable π-coordinated BT complexes: $(\eta^6\text{-}BT)Cr(CO)_3$,[73] $(\eta^6\text{-}BT)\text{-}RuCp^+$,[33] and $Cp^*M(\eta^6\text{-}BT)^{2+}$ (M = Rh, Ir).[33] NMR studies indicate that the metal is coordinated to the benzene ring in all compounds, and this has been established unequivocally by an X-ray diffraction study[33] of $(\eta^6\text{-}BT)RuCp^+$. Attempts to favor coordination of the thiophene ring by using benzothiophenes with methyl substitution in the 2,3-positions of the thiophene ring yielded only the benzene-coordinated complexes $Cp^*Ir(\eta^6\text{-}3\text{-MeBT})^{2+}$ and $Cp^*Ir(\eta^6\text{-}2,3\text{-Me}_2BT)^{2+}$. Thus, in all of the known π-complexes of BT, the benzene ring is the preferred site of metal coordination.

Since the π-thiophene complex $(\eta\text{-}T)RuCp^+$ was so successful (Figure 1) in explaining patterns of deuterium exchange in thiophene on HDS catalysts, similar studies were done with benzo[*b*]thiophene.[74] The OD⁻-catalyzed exchange of benzothiophene protons in $(\eta^6\text{-}BT)RuCp^+$ in CD_3OD at 23.8 °C is first order in the Ru complex and in OD⁻, which suggests a mechanism as proposed for $(\eta\text{-}T)RuCp^+$ (eq 4) involving rate-determining proton abstraction by the base followed by rapid D⁺ addition from the solvent. Fastest exchange occurred at the 2-position (15×10^{-5} M⁻¹ s⁻¹) followed by slower exchange at the 7-position (1.8×10^{-5} M⁻¹ s⁻¹) to give
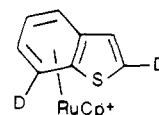
No other protons of the BT ligand exchanged under these conditions. In contrast, deuterium exchange occurring when BT was passed with D_2 over the HDS catalysts, 5% $Re/\gamma\text{-}Al_2O_3$ and $Co_{0.25}MoS$, at 300–400 °C gave preferential exchange at the 2- and 3-positions. Thus, unlike the deuterium exchange studies of the thiophenes, the $(\eta^6\text{-}BT)RuCp^+$ complex is not a useful model for the adsorption and exchange of BT with deuterium. In fact, the exchange of the 2,3-protons suggests that D exchange on the catalyst occurs when BT is coordinated via the thiophene ring, either π-adsorbed or possibly via the S. If the benzene ring of BT is the preferred mode of adsorption on the catalyst, as it is in its metal complexes, it is probably an inactive form. The thiophene-adsorbed form would be active, but relatively little of it would be present, especially if the benzene- and thiophene-adsorbed benzothiophene compete for the same sites. There is, of course, the possibility that the active site is different electronically and/or sterically than the model complexes and preferentially binds to the thiophene ring to promote the exchange. However, at present there is no model complex that reasonably accounts for the observed deuterium exchange of BT on HDS catalysts.

The π-benzene-coordinated BT ligand in $(\eta^6\text{-}BT)\text{-}RuCp^+$ and $Cp^*Ir(\eta^6\text{-}BT)^{2+}$ also does not serve as a useful model for BT HDS.[75] Reactions of these complexes with hydride sources ($HFe(CO)_4^-$, BH_4^-, or

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BEt_3H^-) occur by addition of H^- to the coordinated-benzene carbon atoms. The predominant product is that in which H^- adds to the 7-position (eq 15); however,

(15)
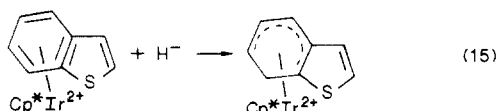
isomers resulting from H^- addition to the 4-, 5-, and 6-benzene ring positions are also observed. As expected, the metal in these complexes activates the benzene ring to react but does not lead to likely HDS intermediates[71] in which C–S bonds are cleaved or the 2,3-positions are hydrogenated.

An interesting reaction with $Fe_3(CO)_{12}$ that does lead to C–S bond cleavage[47] gives a benzothiaferrole product in which a $Fe(CO)_3$ group inserts into a C–S bond (eq 16). Although the low oxidation state of Fe in $Fe_3(C$-

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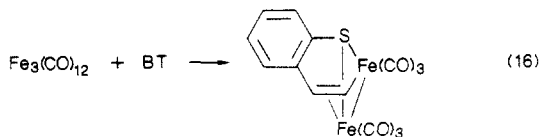
$O)_{12}$ may be more reactive than might be expected of a metal site on an HDS catalyst, especially a Mo-based catalyst, reaction 16 is at present the only model reac-

tion of BT that suggests a reasonable first step in the process. In fact, under $H_2(g)$ at 175 °C, the benzo-thiaferrole in eq 16 gives ethylbenzene, the major product of BT HDS.[71]

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.

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,[1–9] 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 C_2 through 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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