JOURNAL OF CATALYSIS **116**, 11–22 (1989)

Thiophene, 2,3- and 2,5-Dihydrothiophene, and Tetrahydrothiophene Hydrodesulfurization on Mo and Re/γ-Al_2O_3 Catalysts

E. J. MARKEL,* G. L. SCHRADER,*,[1] N. N. SAUER,† AND R. J. ANGELICI†

*Departments of *Chemical Engineering and †Chemistry, and Ames Laboratory, USDOE, Iowa State University, Ames, Iowa 50011*

Received March 21, 1988; revised August 2, 1988

Comparative studies of the hydrodesulfurization (HDS) of thiophene, 2,3-dihydrothiophene, 2,5-dihydrothiophene and tetrahydrothiophene were performed using Mo/γ-Al_2O_3 and Re/γ-Al_2O_3 catalysts. Reaction pathways for interconversion of the organosulfur compounds were shown to exist. Both dihydrothiophene compounds were highly reactive and formed significant amounts of 1,3-butadiene at 300°C over Re catalysts. The dihydrothiophenes are proposed to be possible reaction intermediates for thiophene HDS. © 1989 Academic Press, Inc.

1. INTRODUCTION

Thiophene is representative of the organosulfur compounds found in crude oil which must be removed by hydrodesulfurization (HDS) prior to the production of fuels or petrochemicals. Because of its relatively low reactivity toward HDS, thiophene has been studied extensively. However, uncertainty remains regarding the mechanism of thiophene HDS, particularly the role of hydrogenated thiophene compounds such as the dihydrothiophenes (DHTs) and tetrahydrothiophene (THT). An important question is whether ring hydrogenation occurs prior to C–S bond cleavage or whether direct elimination of sulfur is possible.

In the early 1960s Owens and Amberg (*1–3*) published a series of papers on thiophene HDS for chromia/Al_2O_3 and Co–Mo/Al_2O_3 catalysts. At low hydrogen pressures and at low conversions, small amounts of 1,3-butadiene could be observed using the chromia catalysts; no THT or butanethiol was detected. Analysis of the desulfurized products (butane, 1-butene, *cis*- and *trans*-2-butene) revealed that 1-butene was present in excess of equilibrium amounts. The initial step in hydrodesulfurization was believed to involve the formation of 1,3-butadiene which rapidly underwent hydrogenation to form 1-butene; subsequent hydrogenation and isomerization yielded the observed C_4 product distribution. Desikan and Amberg (*4, 5*) also performed studies with THT and 2,3-dihydrothiophene (2,3-DHT). Thiophene was observed as a reaction product, and a reaction pathway from THT (presumably involving 2,3-DHT) to thiophene was believed to exist. However, because there were differences in the product distributions for thiophene and THT and because butanethiol was observed only for HDS of the hydrogenated thiophenes, Desikan and Amberg postulated different pathways for thiophene and THT HDS.

Kolboe (*6*) investigated the catalytic conversion of thiophene, THT, and *n*-butanethiol over MoS_2, Co-Mo/γ-Al_2O_3, and chromia catalysts. Kolboe also detected no organosulfur products at low hydrogen pressures and low conversions. The amount of 1,3-butadiene produced from THT exceeded that produced from thiophene for all catalysts. Kolboe proposed that it was unlikely that thiophene or THT reacted via hydrogenation or dehydrogenation to form a common surface intermediate; rather a β-elimination pathway involv-

---

[1] To whom correspondence should be addressed.

0021-9517/89 $3.00

ing intramolecular dehydrosulfurization was proposed. In this mechanism, C–S bond cleavage occurs by the transfer of hydrogen from carbons beta to the sulfur. For thiophene HDS, the resultant surface intermediate is diacetylene; for THT HDS, the intermediate is 1,3-butadiene. The adsorbed diacetylene or 1,3-butadiene species were assumed to undergo rapid hydrogenation.

Kolboe's proposals were supported by the infrared work for thiophene on MoS_2 by Ratnasamy and Fripiat (*7*) who assigned a band at 3140–3160 cm^{-1} to an acetylene species. Mikovsky and Silvestri (*8*) performed deuterodesulfurization of thiophene on MoS_2 and concluded that the results were supportive of an acetylenic intermediate. However, other workers such as Zdrazil (*9*) pointed out that the β-elimination pathway is in contradiction with the products observed for HDS of compounds such as 3-methylthiophene. Furthermore, desulfurization of benzothiophenes by this pathway would require the formation of benzyne intermediates which are highly unstable species.

Other results have been consistent with proposed mechanisms involving hydrogenation of thiophene prior to desulfurization. Kieran and Kemball (*10*) examined thiophene and THT HDS using MoS_2 and WS_2 catalysts. They proposed a complex reaction pathway involving hydrogenated surface intermediates. In the initial stages of this mechanism, thiophene undergoes hydrogenation establishing an equilibrium condition on the surface with adsorbed DHT and THT species. Direct desulfurization of THT is not believed to be the predominant reaction pathway; rather partially hydrogenated intermediates are proposed to be activated for desulfurization. As evidence for the importance of hydrogenated species, Kieran and Kemball point to the presence of THT in the thiophene HDS effluent and to the production of more butadiene from THT than from thiophene.

Devanneaux and Maurin (*11*) also observed THT in the product stream of thiophene HDS studies which were conducted at higher H_2 pressures. A two-path mechanism was proposed in which thiophene could react either by hydrogenation to give THT which would subsequently desulfurize or by hydrogenolysis to give desulfurization products as in the Amberg mechanism. Two different catalytic sites—one for hydrogenation and one for hydrogenolysis—were proposed. This was consistent with the observation by Desikan and Amberg (*5*) that pyridine inhibits the hydrogenation activity of the cobalt molybdate catalysts much more than it does the HDS activity.

Zdrazil (*9*) found from the examination of C–S bond strengths that direct cleavage of the aromatic C–S bond in thiophene would be difficult. Disruption of the aromaticity by hydrogenation would make ring cleavage much more likely.

Because of the potential importance of hydrogenated thiophenic species in the HDS of thiophene, we have performed reaction studies involving 2,3-DHT, 2,5-DHT, and THT. Previous studies of THT have been performed (*4, 6, 10*), but only one study of 2,3-DHT has been reported using a cobalt molybdate catalyst (*4*). There have been no reports of 2,5-DHT HDS. The studies were performed using Re/γ-Al_2O_3 and Mo/γ-Al_2O_3 catalysts. The Re catalysts were particularly interesting because of the observation of the partially hydrogenated compounds in the product distribution. New information concerning possible HDS reaction pathways for these organosulfur compounds has been obtained.

2. EXPERIMENTAL PROCEDURE

Preparation of Organosulfur Compound Feedstocks

Thiophene ("99%") and THT ("99%") were obtained from Alfa products and were used without further purification; gas chromatographic analysis confirmed that impurities were less than 0.3%. The 2,3-DHT (*12*) and 2,5-DHT (*13*) were prepared as described previously. To minimize decomposition of the relatively unstable 2,3-DHT, fresh samples were prepared before each reactor run and were stored under N_2 in a liquid N_2 bath prior to use. The 2,5-DHT was much less susceptible to thermal decomposition or oxidation in air and could be prepared in advance and stored at −20°C under N_2 for up to 1 week. ^1H NMR (20°C) indicated purities greater than 97% for both dihydrothiophene compounds.

Catalyst Preparation

Mo/γ-Al_2O_3 catalysts were prepared by the aqueous impregnation of ammonium heptamolybdate onto a calcined γ-Al_2O_3 support (Armak 03-331, 175 m^2/g). A metal weight loading of 5 wt% was used. After vacuum drying for 4 h at 120°C, the catalyst was calcined for 4 h in O_2 at 400°C and was reduced in H_2 for 4 h at 400°C. The reduced catalyst was sieved to produce 50/100 mesh particles.

Re/γ-Al_2O_3 catalysts were prepared (*14*) by the aqueous impregnation of Re_2O_7 onto the calcined γ-Al_2O_3 support. The Re_2O_7 concentration of the impregnation solution was selected to produce a 5 wt% metal loading. The impregnated catalyst was vacuum dried 12 h at room temperature and then slowly reduced in H_2 (2°C/min to 400°C). The reduced catalyst was pressed into pellets (15,000 psi), crushed, and sieved to produce 50/100 mesh particles for charge to the reactor.

Sulfiding of the Re and Mo catalysts was conducted in the reactor using a flowing stream of 1.5 mol% thiophene in H_2 for 4 h at 400°C.

HDS of 2,3-DHT, 2,5-DHT, THT, and Thiophene

Reactor studies (*14*) were performed using a continuous flow fixed bed reactor constructed of $\frac{1}{16}$-in.-i.d. stainless-steel tubing. Approximately 0.122 g of catalyst was packed into the reactor. The flow rate through the reactor was 30 ml/min for all runs. Reactor operating pressures were near atmospheric. A syrine pump (Sage Instruments) was used to inject liquid reactants into a heated 10-in. length of 1-in.-diameter tubing which allowed for complete volatilization and mixing with the H_2. Organosulfur compound concentrations were 1.5 mol% in H_2. Reactor operation was determined by a manifold of zero volume chromatography valves allowing operation in pulse or continuous flow modes.

Gas chromatographic analysis was performed using a dual-column Perkin–Elmer Sigma 4 instrument equipped with an FID detector. A 12-ft Porapak Q column operating at 120°C at 50 ml/min He carrier flow rate was used for the determination of overall reactant conversion and for analysis of thiophene, the dihydrothiophenes, and THT. An 18-in. picric acid on Carbopak C column operating at 120°C and 50 ml/min He carrier flow rate was used to separate the C_4 hydrocarbon products. Separation of 2,5-DHT and THT could not be accomplished using the Porapak Q column. Analysis for these compounds was achieved with ^1H NMR using a Nicolet NT-300 spectrometer. Samples containing thiophene, 2,3-DHT, 2,5-DHT, and THT were collected at −78°C in a removable quartz tube attached to the reactor vent line. The trap, which could be removed under H_2 flow, was kept at −78°C until samples were analyzed by ^1H NMR.

All hydrodesulfurization reactor runs were initiated after the 4-h sulfiding pretreatment. Desulfurization activity after this period was observed to be stable; deactivation was minimal, regardless of subsequent operations. After reactor temperatures were changed, a $\frac{1}{2}$-h stabilization period was permitted before product analysis. If a hydrothiophene was to be studied, the catalyst was brought on-stream in thiophene prior to the introduction of the hydrothiophene. Typically a period of $1\frac{1}{2}$ h was required to flush thiophene from the feed system. After all hydrothiophene reaction studies, the catalyst stability was checked by again performing thiophene HDS. In all cases, deactivation was less than about 10%. The thiophene HDS activity of the γ-Al_2O_3 support at 400°C was negligible (approximately 0.6% conversion). Thermal decomposition of 2,3-DHT during its short residence in the reactor was below detection limits even at 400°C.

Deuterodesulfurization of 2,3-DHT and 2,5-DHT

Deuterodesulfurization runs were performed using the same reactor system. The 5 wt% Re/γ-Al_2O_3 catalyst was used at 400°C and was brought on-stream using a flow of 1.5 mol% thiophene in H_2 for 4 h. After the catalyst activity was confirmed, the feed was switched to 2,3-DHT or 2,5-DHT; activity was again checked after a 2-h stabilization period. The carrier gas was then changed to D_2 (Air Products, Research Grade, 99.99%) and deuterium-exchanged products were collected after 1 h.

Mass spectral data for each component were obtained using a Finnigan 4000 GC-MS at a low ionization energy of 12 eV to reduce total fragmentation to levels lower than 10% of the molecular ion peak. Fractionation of deuterated isomers on the capillary column required spectral averaging across some product peaks. All deuterium exchange data were corrected by comparison with similar data for unexchanged product samples; this allowed correction for the natural occurrence of deuterium and for fragmentation in the spectrometer (assuming equal probability for hydrogen and deuterium loss).

The corrected mass spectrum for each component on the product stream was expressed as the deuterium distribution. This is a series of numbers $d_0, d_1, d_2, \ldots, d_n$, where d_i is the mole fraction of the component containing i deuterium atoms. From these values an average deuterium number may be calculated,

$$\text{D.N.} = \sum_{i=1}^{N} i d_i,$$

where N is the total number of hydrogen atoms in the molecule.

^1H NMR spectra were obtained using a Nicolet NT-300 spectrometer.

3. EXPERIMENTAL RESULTS

Conversion levels and product distributions for Mo/γ-Al_2O_3 and Re/γ-Al_2O_3 catalysts are summarized in Tables 1–4. Feedstocks consisted of thiophene, the dihydrothiophenes, and THT. The reactor

TABLE 1

Conversions and Product Distributions for 5% Mo/γ-Al_2O_3[a]

Feed	Temp (°C)	Thiophene	THT	2,3-DHT	Desulfurized C_4	C_1–C_3
Thiophene	300	95.1	0.8	—[b]	3.8	0.3
	330	90.5	0.6	—	8.6	0.3
	365	83.5	0.3	—	15.7	0.5
	400	74.7	—	—	24.5	0.8
THT	299	—	96.5	—	2.6	0.9
	330	0.1	88.6	—	10.0	1.3
	365	0.6	67.8	—	29.3	2.3
	400	2.8	8.5	—	81.6	7.2
2,3-DHT	300	6.5	57.8	8.3	22.8	4.7
	330	12.6	38.4	—	42.9	6.2
	365	17.7	15.3	—	60.0	7.0
	400	19.6	3.4	—	68.7	8.3

[a] No 2,5-DHT was detected in these studies.

[b] Denotes below detection limits.

TABLE 2

Desulfurized C_4 Product Analysis, 5% Mo/γ-Al_2O_3

Feed	Temp (°C)	Butadiene	1-Butene	2-Butenes	n-Butane
Thiophene	300	—[a]	19.1	74.4	6.5
	330	—	19.8	73.3	7.0
	365	—	20.5	72.0	7.5
	400	—	21.8	70.3	7.9
THT	299	—	42.7	48.1	9.3
	330	—	35.3	57.6	7.3
	365	—	28.4	66.4	5.5
	400	—	23.3	71.1	5.5
2,3-DHT	300	—	47.1	50.1	2.8
	330	—	22.3	74.2	3.2
	365	—	21.1	74.5	4.3
	401	—	21.8	71.9	6.3

[a] Denotes below detection limits.

temperatures ranged from 300 to 400°C. The molybdenum catalyst was used primarily for comparative purposes, being somewhat more typical of commonly used industrial materials.

Mo/γ-Al_2O_3 Catalysts

Reaction data for thiophene, 2,3-DHT, and THT using the 5 wt% Mo/γ-Al_2O_3 catalyst at 300, 330, 365, and 400°C are given in Tables 1 and 2. No 2,5-DHT was observed as a product in any experiment. The desulfurization conversion levels followed the trend of 2,3-DHT > THT > thiophene. The 2,3-DHT was very reactive, with complete conversion achieved above 300°C; however, both thiophene and THT were observed in the reactor effluent. THT HDS tended to produce small amounts of thiophene, but no dihydrothiophene compounds were detected. THT and thiophene conversion levels dropped to less than 5% at 300°C. Thiophene HDS produced small amounts of THT, except at 400°C. Thiophene clearly was the least reactive compound with only about 25% conversion occurring at the highest temperature. Interconversions between the compounds used as feeds consistently followed a trend that at higher temperatures more thiophene was produced while less THT was produced.

Desulfurized products included C_1–C_3

TABLE 3

Conversions and Product Distributions for 5% Re/γ-Al_2O_3

Feed	Temp (°C)	Thiophene	THT	2,3-DHT	2,5-DHT	Desulfurized C_4	C_1–C_3
Thiophene	300	97.6	—[a]	—	—	2.2	0.2
	400	75.0	—	—	—	23.2	1.8
THT	300	.7	97.0	—	—	1.6	0.7
	400	3.1	34.4	—	—	56.2	6.2
2,3-DHT	300	8.5	32.6	39.6	6.9	11.4	0.4
	400	18.3	—	—	—	74.2	7.5
2,5-DHT	300	19.1	26.2	21.8	13.5	17.6	1.9
	400	25.5	—	—	—	67.7	6.8

[a] Denotes below detection limits.

TABLE 4

Desulfurized C_4 Product Analysis, 5% Re/γ-Al_2O_3

Feed	Temp (°C)	Butadiene	1-Butene	2-Butenes	*n*-Butane
Thiophene	300	—[a]	13.2	64.3	22.5
	400	—	18.1	61.5	19.1
THT	300	—	13.7	57.8	28.5
	400	—	18.2	57.9	23.9
2,3-DHT	300	56.9	16.9	22.2	4.0
	400	—	18.9	63.3	17.7
2,5-DHT	300	63.5	11.8	23.4	1.3
	400	—	21.4	68.6	10.0

[a] Denotes below detection limits.

and C_4 hydrocarbons. The concentrations of these hydrocarbons increased with increasing temperatures. The amount of C_1–C_3 hydrocarbons became quite significant at 400°C for 2,3-DHT and THT. Desulfurized C_4 hydrocarbons (Table 2) included 1-butene, *cis*- and *trans*-2-butene (analyzed together), and *n*-butane; no 1,3-butadiene was observed in any of the experiments. At 400°C the product distributions were very similar for all feeds, generally representing thermodynamic equilibrium of the the butenes (26% 1-butene, 44% *trans*-2-butene, and 30% *cis*-2-butene (*15*)). However, the concentrations of 1-butene for 2,3-DHT and THT studies at 300°C represented "excess" amounts. The C_4 hydrocarbon product distributions and conversions for 2,3-DHT were probably influenced by the production of THT and especially thiophene at the higher temperatures.

Re/γ-Al_2O_3 Catalysts

Conversions to desulfurized products and interconversion among thiophene, 2,3-DHT, 2,5-DHT, and THT using the 5 wt% Re/γ-Al_2O_3 catalyst at 300 and 400°C are given in Tables 3 and 4. Conversion levels generally followed the trend 2,5-DHT > 2,3-DHT > THT > thiophene. Both 2,3-DHT and 2,5-DHT were highly reactive—at 400°C the conversion was complete. Interconversion between the dihydrothiophenes was also observed. THT was produced from both dihydrothiophenes at 300°C, but none was detected at 400°C. Smaller amounts of thiophene were produced; these amounts tended to increase with increasing temperature (as for the Mo/γ-Al_2O_3 catalysts). Thiophene and THT reacted over the Re/γ-Al_2O_3 catalysts much the same as they did over the Mo/γ-Al_2O_3 catalysts with nearly equal conversion levels at 300°C; at 400°C desulfurization of THT was more rapid. Small amounts of thiophene were produced from THT, but the thiophene feeds produced no THT.

In comparison to the Mo/γ-Al_2O_3 studies, the amounts of desulfurized C_1–C_3 products were similar for the Re/γ-Al_2O_3 catalysts. The analyses of the desulfurized C_4 hydrocarbons are given in Table 4. At 300°C, 2,3-DHT and 2,5-DHT produced large amounts of 1,3-butadiene, which had not been observed in previous experiments. Smaller amounts of 2-butenes tended to be observed for 2,3-DHT at 300°C for the Re/γ-Al_2O_3 catalysts than for the Mo catalysts. Generally the Re/γ-Al_2O_3 catalyst produced more *n*-butane than did Mo/γ-Al_2O_3, and the amount of 1-butene relative to the 2-butenes tended to be less. However, the amount of *n*-butane produced from 2,5-DHT tended to be only about one-half that produced from other feeds. The C_4 product distributions for thiophene and 2,3-DHT at 400°C tended to be the most similar. THT

TABLE 5

Deuterium Distribution for 2,3-DHT Reaction over 5% Re/γ-Al_2O_3 at 300°C

	2,3-DHT[a]	2,5-DHT[b]	Thiophene	THT	Butadiene	1-Butene	2-Butene[c]
d_0	30.8	57.0	87.3	39.3	5.1	9.1	2.0
d_1	36.2	17.7	7.0	7.2	2.8	2.8	1.3
d_2	19.1	18.6	5.2	20.3	6.8	3.1	3.2
d_3	10.3	5.4	0.6	23.7	13.6	6.0	8.2
d_4	3.0	1.3	—	6.3	25.6	14.0	17.6
d_5	0.4	—		2.6	30.1	15.0	23.6
d_6	—[d]	—		0.6	16.1	25.1	22.2
d_7				—		19.7	15.4
d_8				—		5.2	6.4
D.N.	1.20	0.76	0.19	1.61	4.06	4.88	5.13

[a] Deuterium concentrated at olefins, predominantly at 4 position.
[b] Most deuterium present at olefinic 3, 4 positions.
[c] Similar results found for *cis* and *trans* isomers.
[d] Denotes below detection limit.

produced more *n*-butane than did the other feeds.

Deuterodesulfurization on Re/γ-Al_2O_3

Deuterium incorporation into the principal reaction products is summarized in Tables 5 and 6 for the deuterodesulfurization of 2,3-DHT and 2,5-DHT at 300°C over Re/γ-Al_2O_3. Shown are the deuterium distributions and mean deuterium numbers derived from mass spectral data for the thiophene homologs, hydrogen sulfide, and the major C_4 products. In addition, deuterium locations deduced from ^1H NMR data are qualitatively summarized. Conversions to desulfurized products and C_4 hydrocarbon distributions were similar to those observed for HDS runs.

The 2,3-DHT reaction resulted in relatively large amounts of deuterium incorpo-

TABLE 6

Deuterium Distribution for 2,5-DHT Reaction over 5% Re/γ-Al_2O_3 at 300°C

	2,5-DHT[a]	2,3-DHT[b]	Thiophene[c]	THT	Butadiene	1-Butene	2-Butenes[d]	H_2S
d_0	97.6	33.0	33.6	52.4	61.6	5.2	4.7	79.2
d_1	2.0	50.1	13.7	6.8	28.7	22.8	21.3	19.1
d_2	0.4	15.9	46.9	16.3	7.75	36.9	41.6	1.7
d_3	—[e]	0.8	5.6	19.4	1.3	23.6	18.0	
d_4	—	0.2	0.2	5.1	0.7	7.4	9.0	
d_5	—	—		—	—	4.0	4.93	
d_6	—	—		—	—	—	0.2	
d_7				—		—	—	
d_8				—		—	—	
D.N.	0.02	0.85	1.24	1.18	0.51	2.18	2.22	0.22

[a] Deuterium concentrated at olefins, predominantly at 4 position.
[b] Most deuterium present at olefinic 3, 4 positions.
[c] Most deuterium at the 2 and 5 (α) positions.
[d] Similar results found for *cis* and *trans* isomers.
[e] Denotes below detection limits.

rated into the C_4 hydrocarbon products. Greater than 85% of the butadiene was d_3–d_6. The 1-butene and the 2-butenes were also heavily deuterated (as was *n*-butane). In contrast the thiophene produced was predominantly d_0, as was nearly 40% of the THT and 60% of the 2,5-DHT. The nondesulfurized 2,3-DHT detected in the reactor effluent also contained considerable amounts of deuterium, particularly d_1–d_3 (about 66%); the amount of d_0 was nearly 30% with only small amounts of d_4–d_8.

The deuterium in the thiophene product was present primarily at the 2 and 5 (α) positions. For the 2,5-DHT product deuterium was present mostly at the 3 and 4 (olefinic) positions. The 2,3-DHT which was not desulfurized had deuterium primarily at the olefinic positions, with a preference for the 4 position.

The 2,5-DHT reaction resulted in a much lower incorporation of deuterium. The butadiene produced contained very little deuterium; less than 10% incorporated more than one deuterium atom. The amount of deuterium incorporated in 1-butene and the 2-butenes was also much lower than that for studies with 2,3-DHT. The THT produced had a slightly decreased level of deuterium incorporation while the thiophene had higher levels with the maximum level for d_2. The 2,3-DHT isomerization product was over 80% d_0–d_1. The hydrogen sulfide produced was nearly 80% d_0. The nondesulfurized 2,5-DHT in the reactor effluent was almost completely d_0.

The deuterium in the thiophene product was present at the 2 and 5 (α) positions. For the nondesulfurized 2,3-DHT, deuterium was incorporated predominantly at the olefinic positions, with a preference for the 4 position.

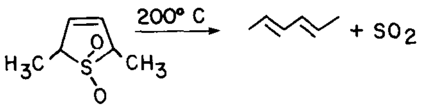
4. DISCUSSION OF RESULTS

The goal of this research has been to develop a better understanding of the role of hydrogenated thiophenes as possible reaction intermediates for thiophene HDS. In doing so we have used two catalysts, Mo/γ-Al_2O_3 and Re/γ-Al_2O_3, and the specific results of these studies were presented above. Now we compare these results noting specific similarities and differences in product formation. Although differences may exist in the mechanisms for the catalysts, disparities in the product distributions may also be due to differences in the relative reaction rates of competing pathways.

Interconversions of thiophene, 2,3-DHT, 2,5-DHT, and THT have been shown to occur. HDS of the dihydrothiophenes over both catalysts indicates a significant conversion to thiophene and THT. Isomerization of 2,3-DHT and 2,5-DHT is also observed over Re/γ-Al_2O_3 catalysts. Mo/γ-Al_2O_3 catalyst studies revealed that interconversion of thiophene and THT can occur. The lower conversions achieved over Re/γ-Al_2O_3 for low temperatures probably place the amounts of THT from thiophene near the detectability limit.

Formation of the dihydrothiophenes from thiophene and THT was not observed; however, such species must certainly be present on the catalyst surface. Since dihydrothiophenes exhibit very high levels of conversion compared to thiophene, their absence from the reactor product effluent for thiophene and THT HDS does not rule out their possible roles as reaction intermediates. The observed trends in thiophene and THT formation from the dihydrothiophenes also support this possibility. The 2,3-DHT and 2,5-DHT react to form thiophene (the most stable organosulfur compound) in relatively greater amounts at higher temperatures while formation of THT decreases with increasing temperature. The same trends are observed for thiophene formation from THT and THT formation from thiophene. 2,3-DHT has been previously suggested as a surface intermediate species for the interconversion of thiophene and THT (*5*).

In many proposed mechanisms for thiophene hydrodesulfurization, the initial C_4 product is butadiene (*1–3, 16*). Large

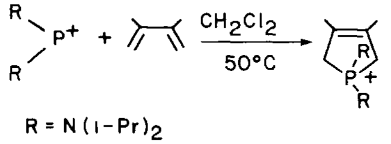


SCHEME 1

amounts of butadiene were observed for the desulfurized products of 2,3-DHT and 2,5-DHT reaction over Re/γ-Al_2O_3 catalysts at 300°C, again supporting the possible role of these compounds as reaction intermediates. The 1-butene concentrations in excess of thermodynamic equilibrium observed for Mo/γ-Al_2O_3 catalysts suggest that butadiene is hydrogenated to produce 1-butene which may subsequently isomerize to form 2-butenes or which may further undergo hydrogenation to form *n*-butane. Differences in C_4 hydrocarbon product distributions for HDS of thiophene and THT compared to HDS of the dihydrothiophenes at 300°C probably reflect the rate of the desulfurization reaction relative to the rates of the hydrogenation and isomerization reactions. At high temperatures (rapid hydrogenation and isomerization) for the Mo/γ-Al_2O_3 catalysts, a near-equilibrium distribution of butene isomers with a small amount of *n*-butane can be produced. However, for Re/γ-Al_2O_3 catalysts at 300°C the desulfurization reactions dominate the C_4 conversions: 1,3-butadiene is observed at high concentrations.

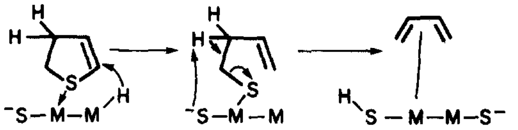
Determination of the relative roles of 2,3-DHT and 2,5-DHT in thiophene HDS is more difficult. In addition to the formation of thiophene and THT from 2,3-DHT over the Re/γ-Al_2O_3 catalyst at 300°C, 2,5-DHT was also produced. This isomerization was not observed previously by Desikan and Amberg (*5*) over Co–Mo/γ-Al_2O_3 catalysts, and it was not observed using the Mo/γ-Al_2O_3 catalysts. A pathway for HDS of 2,3-DHT could involve the isomerization of 2,3-DHT to 2,5-DHT followed by elimination of sulfur to produce butadiene. Reaction of 2,5-DHT over Re/γ-Al_2O_3 catalysts at 300°C produced large amounts of butadiene. The 2,5-DHT was substantially more reactive under these conditions than 2,3-DHT. A similar type of elimination has been reported for several noncatalytic systems. Vapor-phase pyrolysis of 2,5-dihydro–2,5-dimethylthiophene–1,1 dioxide yields a diolefin through the loss of SO_2 (*17*, *18*) (see Scheme 1). In a reverse coupling reaction, phosphonium ions react with 1,3-butadienes resulting in the formation of 3-phospholenium ions (*19*) (see Scheme 2). Both of these reactions are believed to proceed in a concerted manner. The elimination of 1,3-butadiene from 2,5-DHT could proceed in a similar manner (see Scheme 3). This elimination step has also been demonstrated for a transition metal complex, $Fe(CO)_4$ (2,5-DHT), which produced 1,3-butadiene upon thermal decomposition at 120°C (*20*). Butadiene has also been determined to be the primary product in the gas-phase reaction of 2,5-DHT with hydrogen atoms (*21*).

However, none of these results can exclude the possible direct elimination of sulfur from 2,3-DHT. The high desulfurization reactivity of 2,3-DHT makes it likely that at least a portion of the thiophene desulfurizes via a 2,3-DHT intermediate. There also is evidence from the deuterodesulfurization studies that not all of the 1,3-butadiene formed is directly produced from 2,5-DHT. The 1,3-butadiene resulting from the 2,3-DHT feed has a substantially higher deuterium content than that formed from 2,5-



SCHEME 2

SCHEME 3



Scheme 4

DHT feeds, with 75% of the product being d_3–d_5. Much of this deuterium could have been incorporated through initial deuterium exchange of the 2,3-DHT. The 1,3-butadiene which is almost entirely deuterated, however, probably was not formed from 2,5-DHT directly. Another pathway for 1,3-butadiene production must exist. Because nearly 90% of the unreacted 2,3-DHT is d_0–d_2, the large amounts of deuterium must have been incorporated after an irreversible step, such as C–S bond cleavage. The resultant intermediate would undergo exchange and then eliminate sulfur to form 1,3-butadiene. For complexes such as [CpRu(η-thiophene)] BF_4 (and for complexes involving 2-methylthiophene, 3-methylthiophene, 2,3-dimethylthiophene, 2,3,4-trimethylthiophene, or 2,3,5-trimethylthiophene), attack by a hydride results in C–S bond cleavage to produce a butadienethiolate (*22*). It is possible that a similar type of reaction could occur at the olefin in 2,3-DHT (see Scheme 4). If hydride attack causes ring cleavage, the intermediate would still need to be deprotonated prior to sulfur elimination to form 1,3-butadiene as the product. This deprotonation of the less acidic β-hydrogens could cause this step to be slow (rate determining); this may allow the intermediate to undergo H–D exchange.

The extent of deuterium incorporation into the dihydrothiophenes and the desulfurized products may be understood as follows. The products of the reaction of 2,5-DHT over Re/γ-Al_2O_3 at 300°C contain very small amounts of deuterium. Unreacted 2,5-DHT is nearly completely unexchanged (97.6% d_0) under these conditions. The 1,3-butadiene produced is 90% d_0 or d_1, as would be expected from direct elimination. The relatively small amounts of deuterium incorporated could readily result from exchange of the 1,3-butadiene product. Hydrogenation of 1,3-butadiene over a supported Re catalyst has been examined previously (*23*); deuterium tracer studies showed that 40% d_1 or d_2 is produced. In contrast unreacted 2,3-DHT does undergo H–D exchange over the Re catalyst under similar conditions. While 30% of the unreacted 2,3-DHT was d_0, 36% was d_1, 20% was d_2, 10% was d_3, and 3% was d_4. ^1H NMR revealed that about 80% of the deuterium was concentrated at the olefinic positions of the 2,3-DHT. Hydrogens adjacent to heteroatoms are more acidic than those beta to sulfur and are more readily deprotonated by lithium reagents and other strong bases (*24, 25*). If hydrogen exchange by the catalysts involves the initial deprotonation by a basic surface group followed by deuteration by an S–D group—as has been previously suggested (*26*) for thiophene exchange with D_2 over HDS catalysts—then the more acidic a hydrogen, the more likely that it will undergo exchange. Thus, 2,3-DHT would be expected to incorporate larger amounts of deuterium than 2,5-DHT, and the HDS products would have a larger deuterium content. Similarly, the 2,5-DHT formed from 2,3-DHT was nearly 45% d_1, d_2, or d_3; but when 2,5-DHT was the reactor feed, it was 97.6% d_0.

Other results of the deuterodesulfurization studies are also interesting. The H_2S formed from deuterodesulfurization of 2,5-DHT contained almost no deuterium. For thiophene, other workers (*8, 16*) have observed primarily H_2S and have proposed that H_2S is formed because large amounts of hydrogen are exchanged by the thiophene onto the catalyst surface. Cowley observed that while only small amounts of thiophene were desulfurized over Co–Mo/γ-Al_2O_3 catalysts, nearly 100% of the α-hydrogens of the thiophene feed were exchanged, thus replacing the surface deuterium, leaving a "pool" of surface hydrogen. While exchange of the 2,5-DHT and its desulfurization products was not as extensive as for thiophene, it is quite possible that a surface pool of hydrogen left by exchange is at least in part responsible for the observation of H_2S rather than D_2S. However, it is likely that in addition to this factor, an isotope effect makes the rate of reaction for hydrogen on the catalyst surface faster than that for deuterium. Thus H_2S is the main product.

Small amounts of deuterium in the THT produced were also observed. Formation of THT from either 2,5-DHT or 2,5-DHT necessitates the addition of two hydrogens or deuteriums; under D_2, therefore, it might be expected that the THT formed should be primarily d_2 or higher. However, for reaction of both dihydrothiophenes, the THT was primarily d_0. This could result only if a significant amount of thiophene was on the surface or if the rate of transfer of hydrogen from either a M–H or S–H was faster than that from M–D or S–D, that is, a kinetic isotope effect. Deuterium isotope effects ranging from 2 to 5 have been reported for heterogeneous systems (*27–29*), although these studies have primarily involved C–H bond breaking reactions rather than HDS. No studies of deuterium isotope effects over sulfided metal catalysts have been reported in the literature; however, the theoretical maximum isotope effect for breaking a S–H bond is 5.4 and for breaking a M–H bond is 4.2 (*30*).

5. CONCLUSIONS

Both 2,3-DHT and 2,5-DHT were observed to be much more reactive than thiophene and tetrahydrothiophene over $Mo/\gamma\text{-}Al_2O_3$ and $Re/\gamma\text{-}Al_2O_3$ catalysts. Interconversions between the organosulfur compounds were observed. Desulfurization of 2,5-DHT yields butadiene directly. Deuterodesulfurization experiments indicated that 2,3-DHT can also desulfurize to form 1,3-butadiene. Hydrogenation produces 1-butene which can then isomerize to form the 2-butenes. On the basis of these results and additional work involving model organometallic compounds, it has been possible to propose a more comprehensive mechanism for thiophene HDS (*20*).

ACKNOWLEDGMENTS

This work was conducted through the Ames Laboratory which is operated for the U.S. Department of Energy by Iowa State University under Contract W-7405-ENG-82. This work was supported by the Office of Basic Energy Sciences.

REFERENCES

1. Owens, P. J., and Amberg, C. H., *Adv. Chem. Ser.* **33,** 182 (1961).
2. Owens, P. J., and Amberg, C. H., *Canad. J. Chem.* **40,** 941 (1962).
3. Owens, P. J., and Amberg, C. H., *Canad. J. Chem.* **40,** 947 (1962).
4. Desikan, P., and Amberg, C. H., *Canad. J. Chem.* **41,** 1966 (1963).
5. Desikan, P., and Amberg, C. H., *Canad. J. Chem.* **42,** 843 (1964).
6. Kolboe, S., *Canad. J. Chem.* **47,** 352 (1969).
7. Ratnasamy, P., and Fripiat, J. J., *Trans. Faraday. Soc.* **66,** 2897 (1970).
8. Mikovsky, R. J., and Silvestri, A. J., *J. Catal.* **34,** 324 (1974).
9. Zdrazil, M., *Collect. Czech. Commun.* **40,** 3491 (1975).
10. Kieran, P., and Kemball, C., *J. Catal.* **4,** 394 (1965).
11. Devanneaux, J., and Maurin, J., *J. Catal.* **4,** 394 (1981).
12. Sauer, N. N., Angelici, R. J., Huang, Y. C. J., and Trahanovsky, W. S., *J. Org. Chem.* **51,** 113 (1986).
13. Everhardus, R. H., Grafing, R., and Brandsma, L., *Recueil J. R. Neth. Chem. Soc.* **95,** 153 (1976).
14. Markel, E. J., M. S. thesis, Iowa State University, Ames, 1986.
15. Benson, S. W., and Bose, A. W., *J. Amer. Chem. Soc.* **85,** 1385 (1963).
16. McCarty, K. F., and Schrader, G. L., *J. Catal.* **103,** 261 (1987).
17. Mock, W. L., *J. Amer. Chem. Soc.* **88,** 2857 (1966).
18. McGregor, S. D., and Lemal, D. M., *J. Amer. Chem. Soc.* **88,** 2858 (1966).
19. Cowley, A. H., Kemp, R. A., Lasch, J. G., Norman, N. C., Stewart, C. A., and Wittlesey, B. R., *Inorg. Chem.* **25,** 740 (1986).
20. Sauer, N. N., Angelici, R. J., and Markel, E. J., and Schrader, G. L., submitted for publication.
21. Horie, O., Nishino, J., and Amano, A., *J. Org. Chem.* **43,** 2800 (1978).
22. Hachgenei, J. W., and Angelici, R. J., *Angew. Chem. Int. Ed. Engl.* **26,** 909 (1987).

23. Grant, J., Moyes, R. B., and Wells, P. B., *J. Catal.* **51,** 355 (1978).

24. Tagaki, W., *in* "Organic Chemistry of Sulfur" (S. Oae, Ed.), Chap. 6. Plenum, New York, 1977.

25. Oshima, K., Shimoji, K., Takahashi, H., Yamamoto, H., and Nozaki, H., *J. Amer. Chem. Soc.* **95,** 2694 (1973).

26. Sauer, N. N., and Angelici, R. J., *Organometallics* **6,** 1146 (1987).

27. Machiels, C. J., and Sleight, A. W., *J. Catal.* **76,** 238 (1982).

28. Manogue, W. H., and Groff, R. P., *J. Catal.* **87,** 461 (1984).

29. Hardee, J. R., and Hightower, J. W., *J. Catal.* **86,** 137 (1984).

30. Moore, J. W., and Pearson, R. G., "Kinetics and Mechanisms," 3rd ed., pp. 367–370. Wiley, New York, 1981.