

Studies of the mechanism of thiophene hydrodesulfurization: ^2H NMR and mass spectral analysis of 1,3-butadiene produced in the deuterodesulfurization (DDS) of thiophene over PbMo_6S_8 catalyst

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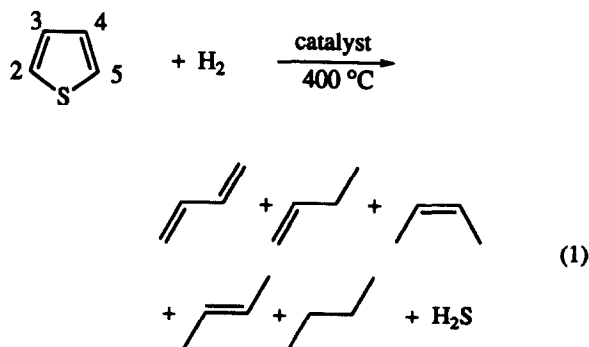
Abstract

The deuterodesulfurization (DDS) of thiophene was investigated over PbMo_6S_8 at 400°C using a flow-microreactor. Evidence indicates that 1,3-butadiene (BDE) is the first desulfurized product; its deuterium content was established by ^2H NMR and mass spectrometries. At different levels of thiophene conversion (0.86–10.2%), the amount of deuterium incorporated into BDE remains constant at 3.47 D atoms per BDE molecule. Unconverted thiophene incorporates 0.42 D atoms at 10.2% thiophene conversion but only 0.05 D atoms at 0.86% conversion. Reaction of 2,5-dihydrothiophene (2,5-DHT) with D_2 at 400°C over PbMo_6S_8 liberates BDE as the only hydrocarbon product. This BDE incorporates no deuterium. Thiophene and H_2S effectively inhibit both BDE hydrogenation and deuterium exchange. The results indicate that during the DDS process, a total of 3.2 deuterium atoms are incorporated into the BDE; 0.83 D are in the D_A -position while 1.2 D are in each of the D_B - and D_C -positions. Several HDS mechanisms proposed in the literature are consistent with these results; two are not. Details of all of these mechanisms are discussed.

Keywords: Chevrel phase catalyst; Deuterium labelling; Hydrodesulphurization; Mechanisms; Thiophene

1. Introduction

Catalytic hydrodesulfurization (HDS) is a large-scale industrial process for the removal of sulfur from petroleum feedstocks [1]. Thiophene has been studied extensively as a model for this process. The reaction of thiophene with H_2 over supported HDS catalysts, $\text{Co-Mo}/\text{Al}_2\text{O}_3$, $\text{Ni-Mo}/\text{Al}_2\text{O}_3$ and $\text{Ni-W}/\text{Al}_2\text{O}_3$, produces H_2S and a mixture of four-carbon hydrocarbons [2,3]: 1,3-butadiene, 1-butene, *cis*- and *trans*-2-butene and butane (eq 1). Of the C_4 products,



1,3-butadiene has been suggested as the most likely product formed directly following C–S

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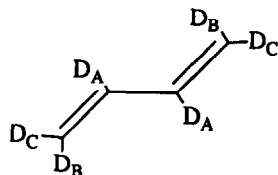


Fig. 1. Structure of 1,3-butadiene (BDE) showing the positions of deuterium incorporation as detected by ^2H NMR.

bond cleavage because it is detected [2–4] under reduced hydrogen pressure where its hydrogenation to butenes and butane is less favorable. Other evidence supports this proposal. First, the relative amount of 1,3-butadiene produced in the HDS of thiophene over MoS_2 [3a] and Chevrel-phase catalysts [4] increases with decreasing thiophene conversion. Second, 1-butene is produced in these reactions in greater than equilibrium amounts (20% 1-butene, 31% *cis*-2-butene, 49% *trans*-2-butene at 400°C , calculated from ΔG_f° values given in [5]), supporting a sequential hydrogenation path from 1,3-butadiene to 1-butene. Direct hydrogenation of 1,3-butadiene over MoS_2 at 320°C also produces excess 1-butene [3]. Studies of 1-butene hydrogenation over several Chevrel-phase catalysts (including PbMo_6S_8) [6] show no evidence of 1,3-butadiene at 400°C in a flow reactor. Thus, it is unlikely that 1,3-butadiene is produced from 1-butene dehydrogenation.

Based on evidence that 1,3-butadiene is likely to be the first HDS product, mechanisms proposed for thiophene HDS often involve pathways leading to its formation. Our approach to testing these

mechanisms is to compare the deuterium content and its location in 1,3-butadiene produced during the deuterodesulfurization (DDS, using D_2 instead of H_2) of thiophene over PbMo_6S_8 at 400°C with that predicted by each mechanism. In order to do the deuterium studies it was necessary to choose a catalyst that produced reasonable amounts of 1,3-butadiene. Since the Chevrel-phase catalyst, PbMo_6S_8 , is a relatively poor olefin hydrogenation catalyst [4,6a], it does indeed yield 1,3-butadiene (6.5% of the C_4 hydrocarbon products). An additional benefit of this catalyst is its low activity toward catalyzing the exchange of hydrogens in thiophene with deuterium [4]; substantial deuterium incorporation into thiophene before the HDS reaction would further complicate interpretation of the deuterium composition of the 1,3-butadiene product. The total amount of deuterium incorporation was determined experimentally by mass spectrometry, and the relative amounts of deuterium incorporated into each of the three distinguishable positions of 1,3-butadiene (D_A , D_B , D_C ; Fig. 1) were determined by integration of their peaks in the ^2H NMR spectrum. Prior to considering the experimental results, it is useful to examine the deuterium content of 1,3-butadiene that would be predicted from mechanisms that have been proposed in the literature. For the remainder of this paper, 1,3-butadiene will be abbreviated BDE.

This analysis of thiophene HDS mechanisms will be limited to those mechanisms that are given

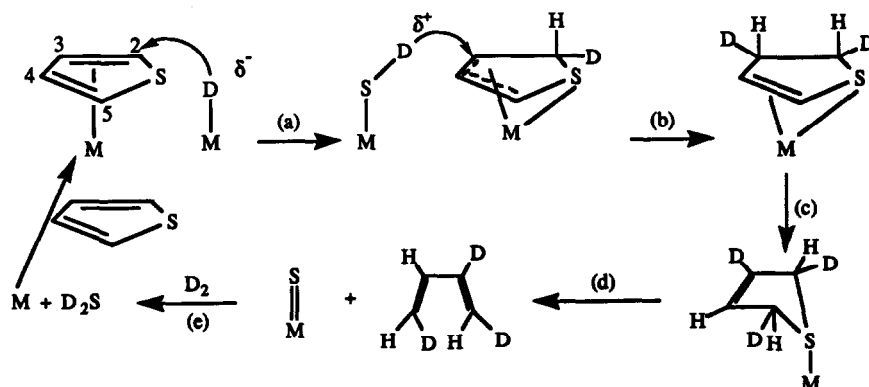


Fig. 2. Hydrogenation mechanism proposed by Sauer, Markel, Schrader and Angelici [7] indicating sites of deuterium incorporation.

in sufficient detail to allow one to predict from them the number and locations of deuterium in the BDE product. One such mechanism (Fig. 2) [7], proposed in these laboratories and based on a series of organometallic and reactor studies, involves partial thiophene hydrogenation. The thiophene adsorbs to a metal site through all five atoms (η^5); this adsorption activates the thiophene to react with a surface hydride at the 2-position (step *a*) to give an allyl sulfide intermediate. A strongly acidic H^+ , perhaps from an $-SH$ group, adds in step *b* to the 3-position forming adsorbed 2,3-dihydrothiophene (2,3-DHT). Isomerization of 2,3-DHT to 2,5-dihydrothiophene (2,5-DHT) (step *c*) is followed by cleavage of both C–S bonds (step *d*) to give BDE and an adsorbed S atom. One equivalent of H_2 removes S as H_2S to regenerate the active site (step *e*). Under DDS conditions, where the amount of D_2 is much greater than that of thiophene, this mechanism predicts the addition of one D atom in each step *a* and *b*. During the isomerization (step *c*), a third D atom is added to the 5-position, while either D or H is lost from the 3-position. The 2,3-DHT formed in step *b* could be bound through both the olefin and the sulfur as shown, or through just the S atom; only sulfur-coordination is observed in its transition metal complexes [8]. In this latter case, either H or D could be lost from the 3-position since either side of the ring can contact the surface as a result of rapid inversion at the sulfur and flipping of the ring. This type of inversion is known to occur in S-coordinated 2,3-DHT complexes [8]. Because the deuterium isotope effect [9] will cause the C(3)–D bond to be stronger than C(3)–H in 2,3-DHT, the 3-position of 2,5-DHT will probably contain more D than H. An estimated k_H/k_D isotope effect of 2.3 at 400°C is calculated from the difference in zero point energies for C–H and C–D bonds [9a]; this leads to 0.70 D atoms at C(3) of the 2,5-DHT. An isotope effect has been measured [9b] for H vs. D abstraction from CH_3CD_3 by $\cdot CH_3$ at 401°C; this k_H/k_D value (3.33) predicts 0.77 D atoms at C(3) in 2,5-DHT. Both estimates of k_H/k_D lead to similar estimates of the

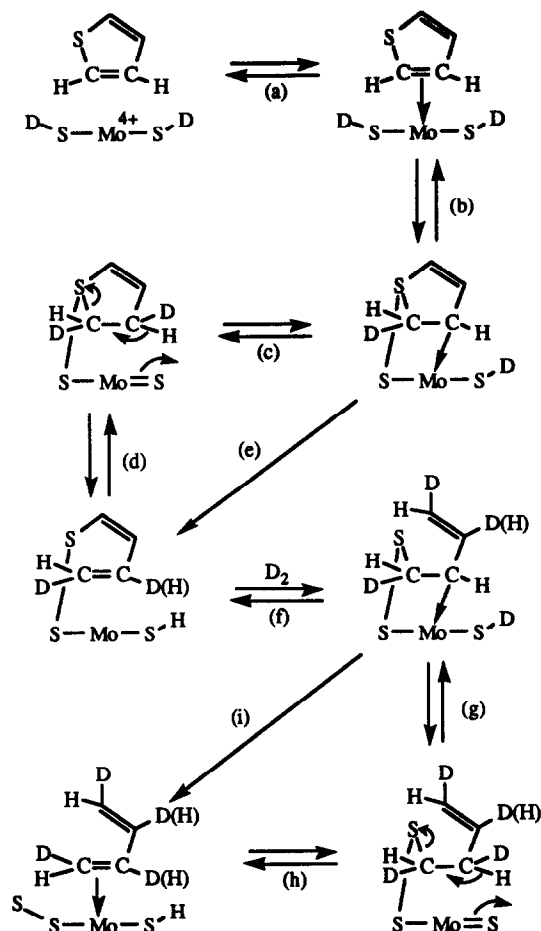


Fig. 3. Multipoint mechanism proposed by Kwart, Schuit and Gates [10] indicating sites of deuterium incorporation.

deuterium content (0.70 or 0.77 D) at C(3) of 2,5-DHT. Using the 0.77 D value, the entire 2,5-DHT will contain approximately 2.8 D. In the desulfurization step (*d*), no deuterium is incorporated and the resulting BDE should contain 2.8 D, and these deuterium atoms should be distributed (Fig. 1) as follows: 0.77 D at D_A , 1.0 D at D_B , and 1.0 at D_C . (It is not possible to predict whether the deuterium content at D_B and D_C will be equal or unequal.)

A second mechanism involving partial hydrogenation of thiophene was proposed by Kwart, Schuit and Gates (Fig. 3) [10]. The first step of this mechanism (step *a*) is η^2 -coordination of thiophene through one of its double bonds to a surface metal atom. As the thiophene S atom interacts with a nearby surface S atom, one H atom adds to

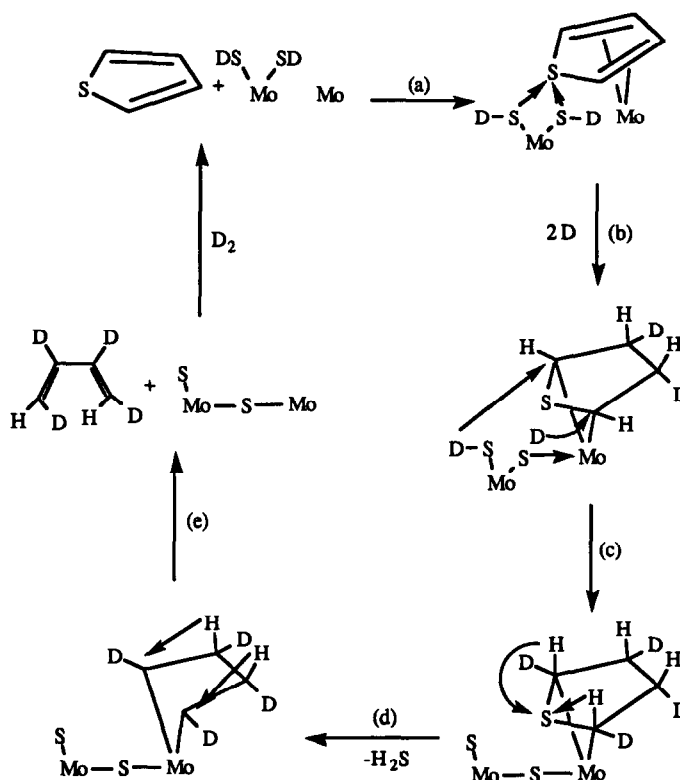


Fig. 4. HDS mechanism proposed by Delmon and Dallons [11] indicating sites of deuterium incorporation.

C2 (step *b*). Next, either another H atom adds to give a 2,3-DHT intermediate bound through only the S atom (step *c*) followed by β -elimination and C2–S bond cleavage (step *d*) to give an adsorbed butadiene thiolate, or the butadiene thiolate is formed directly (step *e*) without addition of the second proton. The authors are undecided as to which path (steps *c* and *d*, or step *e*) would be favored or whether both occur simultaneously. Repetition of these steps (steps *f*, *g* and *h* or steps *f* and *i*) at the other double bond cleaves the second C–S bond and gives adsorbed BDE as the final product.

Under DDS conditions, formation of the 2,3-DHT intermediate (steps *b* and *c*) requires addition of two D atoms. Again, as in Fig. 2, H would transfer more rapidly to the surface than deuterium during the β -elimination step *d*. On the other hand, step *e* requires addition of only one D atom. Repetition of these steps at the second C–C double bond gives BDE with either 0.0 D atoms at the

D_A -positions by paths *e* and *i* or 1.54 D, based on the 3.33 k_H/k_D isotope effect [9a], at the D_A -position by paths *c*, *d*, *g* and *h*. Both pathways introduce a total of two D atoms at the D_B - and D_C -positions for a total of 2.0–3.5 D in the product BDE.

A third hydrogenation mechanism (Fig. 4) was proposed by Delmon and Dallons [11]. In this mechanism, thiophene is initially η^4 -bound through the π -system to a coordinatively unsaturated surface metal atom while the thiophene S atom acts as a Lewis acid toward the S atoms of neighboring surface –SH groups (step *a*). Such an intermediate seems unlikely since the sulfur in known η^4 -coordinated thiophene complexes is a strong Lewis base [12], rather than a Lewis acid. Two H atoms add in step *b* to saturate C3 and C4 as C2 and C5 form σ -bonds with the metal atom. Transfer of H atoms from the surface –SH groups to C2 and C5 creates two hypervalent carbons in a transition state (step *c*) which lose the two orig-

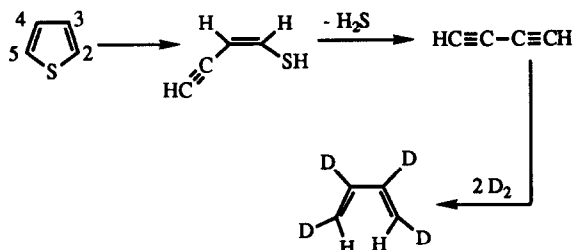


Fig. 5. Dehydrodesulfurization mechanism proposed by Kolboe [13].

inal thiophene protons to the thiophene S atom to give H_2S (step *d*). Under low H_2 pressure, hydrogens from C3 and C4 migrate to C2 and C5 (step *e*) and BDE is desorbed from the surface. Under DDS conditions, this mechanism adds two D atoms to C3 and C4 in step *b*. Step *c* adds two more deuterium atoms from the surface to C2 and C5 as H_2S is lost in step *d*. Migration of hydrogens from C3 and C4 to C2 and C5, desorbs BDE with four D atoms. According to the isotope effect [9a], 1.54 D atoms will remain at the D_A -position of BDE (Fig. 1), and 2.5 D atoms will occupy the D_B - and D_C -positions. The total number of D atoms in the BDE product would be 4.0.

Kolboe [13] proposed dehydrodesulfurization as the initial step (Fig. 5) in his mechanism. It involves stepwise elimination of H3 and H4 which promotes C–S bond cleavage to give H_2S and 1,3-butadiyne. Two equivalents of H_2 hydrogenate 1,3-butadiyne to give BDE. Two equivalents of D_2 during DDS would produce 1,3-butadiene- d_4 . Two D atoms would be in the D_A -positions of BDE and two would be in the D_B - and D_C -posi-

tions (Fig. 1). Again, it is not possible to ascertain from the mechanism whether the two D atoms in the D_B and D_C sites would be equally or unequally distributed between these positions.

Reactions of the transition metal complex, $\text{Cp}^*\text{Ir}(\eta^4\text{-2,5-dimethylthiophene})$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) provide the basis for an HDS mechanism (Fig. 6) [14] proposed by Chen and Angelici. In this mechanism, thiophene is activated by π -coordination of just the diene fragment of thiophene (η^4) to undergo base-catalyzed (basic Al_2O_3) C–S bond cleavage (step *a*), forming a six-membered ring. Coordination of an adjacent surface metal atom to the sulfur (step *b*) cleaves the second C–S bond (step *c*) forming a metallacyclopentadiene. Addition of one equivalent of H_2 eliminates H_2S (step *e*); a second equivalent of H_2 cleaves the M–C bonds and desorbs BDE (step *f*). Deuterium incorporation into BDE during DDS would occur only during step *f*, giving 1,3-butadiene- d_2 . This mechanism predicts that deuterium would occupy only the D_B - and D_C -positions (Fig. 1) with no deuterium incorporation at the D_A -position.

Other mechanisms for thiophene HDS, which lead to butadiene- d_2 with the deuterium in only the D_B - and D_C -positions and involve C–S bond hydrogenolysis prior to hydrogenation of the unsaturated hydrocarbon part of thiophene have also been proposed. Differing in the initial coordination mode and subsequent reactions, mechanisms by Desikan and Amberg [15], Lipsch and Schuit [16], Curtis [17] and Cowley [18] all add two equivalents of H_2 to cleave the C–S bond to

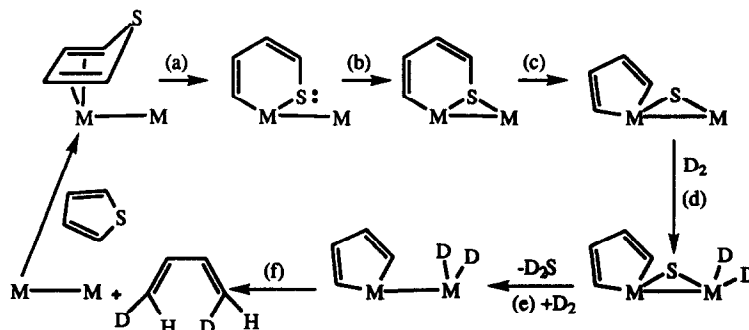


Fig. 6. C–S cleavage mechanism proposed by Chen and Angelici [14] indicating deuterium incorporation into butadiene (BDE).

Table 1
Deuterium numbers (D.N.) and deuteration sites predicted by various mechanisms for deuterodesulfurization

Mechanism Fig. no.	D.N.	D _A	D _B and D _C	Ref.
2	2.8	0.77	2.0	[7]
3	2.0–3.5	0.0–1.5	2.0	[10]
4	4.0	1.5	2.5	[11]
5	4.0	2.0	2.0	[13]
6	2.0	0	2.0	[14]

produce BDE and H₂S. During DDS of thiophene by these mechanisms, only the D_B- and D_C-positions of 1,3-butadiene-d₂ would have D atoms, and there would be a total of only two D atoms in those positions.

Table 1 summarizes the number of deuterium atoms (deuterium number, D.N.) and their locations (D_A, D_B, or D_C, Fig. 1) predicted for each of the mechanisms discussed in detail above. Deuterium numbers range from 2 to 4; a total of at least two D atoms are in the D_B- and D_C-positions for all mechanisms (the mechanisms are unclear as to whether D_B or D_C would be favored). On the other hand, the number of D atoms in the D_A-position varies from 0 to 2. Thus, the amount of deuterium in the D_A-positions as well as the total number of deuterium atoms (D.N.) distinguish several of the mechanisms from each other. Experimental measurements of D.N. and deuterium location in the BDE should allow us to narrow the number of mechanisms that are possible during HDS under the conditions of our studies.

In the present study, we examined the deuterium content and location in BDE produced during thiophene DDS over the Chevrel-phase catalyst PbMo₆S₈ at 400°C [4]. The deuterium (D.N.) of the BDE produced in this reaction as determined by mass spectrometry gave the average number of D atoms per molecule of BDE. The relative amounts of deuterium at each position (D_A, D_B, or D_C) of the 1,3-butadiene were determined by integrating the peaks in the ²H NMR spectrum. The results were used to evaluate the viability of each of the mechanisms discussed above. In the course of these studies, it became necessary to also investigate reactions of D₂ with BDE, 2,5-DHT

and H₂S under the same conditions as the thiophene HDS studies; all of these results are reported herein.

The more saturated 1- and 2-butene products of thiophene DDS over PbMo₆S₈ contained [4] much higher levels of deuterium (D.N. = 5.36 to 5.54), presumably because they form as a result of deuteration of the initially formed 1,3-butadiene. Since these butenes were formed in subsequent reactions of BDE, their deuterium content was not of direct relevance to the HDS mechanism and therefore was not investigated in this study.

2. Experimental

2.1. Preparation

The Chevrel catalyst, PbMo₆S₈, was prepared as previously described [6b]; characterization by X-ray diffraction was carried out to determine the bulk purity of the catalyst on a Siemens D500 diffractometer using CuKα radiation. Raman spectroscopy was performed on a Spex 1403 double monochromator spectrometer which confirmed the absence of MoS₂ (bands at 383 and 409 cm⁻¹) using the 514.5 nm line of a Spectra Physics argon laser operating at 200 mW (measured at the source). The catalyst was crushed and sieved to produce 40–100 mesh particles for all reactions. Surface area measurements were made on the same catalyst particle size, using the BET method on a Micromeritics 2100E Accusorb instrument at liquid nitrogen temperature using Kr as the adsorbing gas. The average surface area was found to be 0.80 ± 0.09 m²/g.

2.2. Reactants

Thiophene (99+%) was purchased from Aldrich and purified as previously described [19]. Deuterium gas (Research grade, 99.99%), hydrogen gas (zero grade, 99.997%) and helium gas (zero grade, 99.997%) were purchased from Air Products. C.P. grade (99.0%) 1,3-butadiene and C.P. grade (99.5%) hydrogen sulfide were pur-

chased from Matheson. The 2,5-dihydrothiophene (2,5-DHT) was prepared by a literature method [20] and found to be greater than 97% pure by ^1H NMR spectrometry.

2.3. Reactor system

Deuterodesulfurization of thiophene and 2,5-dihydrothiophene were performed on a fixed-bed, continuous-flow microreactor similar to that previously described [6]. The reactor bed was constructed from a 1.5 in \times 0.25 in (o.d.) stainless steel tube. The catalyst was held in place between two pads of quartz wool. The gases, H_2 , D_2 and He, were purified by passing through an oxy-trap (Alltech), 5Å molecular sieves (Alltech), activated charcoal (Alltech) and a 5 μm filter (Alltech). Reactant gases, 1,3-butadiene and H_2S were passed through 5Å molecular sieves and a 5 μm filter. The flow rate through the reactor was 31 ml/min; operating pressure was near atmospheric. A Sage 341B syringe pump was used to inject thiophene and 2,5-DHT from a 2.50 ml gas-tight syringe into a heated saturator (6 in \times 1/2 in stainless steel tubing packed with 5 mm glass beads) to completely volatilize the thiophenes. A series of two 6-port and one 4-port switching valves allowed for pulse- and continuous-flows of reactants over the catalyst as well as reaction stream sampling for GC analysis.

Gas chromatography was used for determinations of percent conversion of thiophene and C_4 product distribution. The GC, a Varian 3400 equipped with an FID detector, was connected to a 6-port valve on the reactor; 1.0 ml gas samples were injected directly from a 1.0 ml sample loop. The separated products were quantified on a Varian 4270 integrator. A 4-port valve and a 10-port valve on the GC allowed for the operation of two separate GC columns and for the reversal of column flow. Percent conversion of thiophene was determined on a 12 in \times 1/8 in (o.d.) stainless steel column packed with Porapak Q (Alltech); the flow through the column was 20 ml/min at 110°C. The C_4 hydrocarbons were separated on a 6 ft. \times 1/8 in. (o.d.) column packed with 0.19%

picric acid on Graphpac GC; the He flow through the column was 40 ml/min. The column temperature was held at 40°C for 5 min followed by a 35°/min ramp to 65°C. After a 2 min hold, a final ramp (35°/min) to 110°C was used as the column flow was reversed to separate thiophene or to remove thiophene and 2,5-DHT (thiophene and 2,5-DHT did not separate on this column).

2.4. Experiment A. Deuterodesulfurization of thiophene

Liquid thiophene was syringed into the reactor system at a rate of 0.12 ml/h (2.5×10^{-5} mol/min); D_2 flow was 31 ml/min (1.3×10^{-3} mol/min). The PbMo_6S_8 catalyst was heated to $400 \pm 1^\circ\text{C}$ in a stream of He (20 ml/min). The saturator, feed lines and valves were heated to $120 \pm 2^\circ\text{C}$ to ensure that thiophene (b.pt. = 84°C) was vaporized. The empty reactor showed no hydrodesulfurization activity. The reactor temperatures were allowed to stabilize for 1 h before the feed stream was brought on-line. Percent conversion and C_4 product distribution were monitored throughout the reaction by GC. Trapping of the reaction products at the vent in a liquid-nitrogen-cooled Pyrex tube containing 5 mm glass beads commenced 15 min after the reactants were brought on-line, and continued for 12 h, the duration of the experiment. The unreacted thiophene and BDE product were analyzed by mass and ^2H NMR spectrometries.

2.5. Experiment B. Deuterodesulfurization of 2,5-DHT

The 2,5-DHT reaction with D_2 over PbMo_6S_8 was conducted in a manner similar to that of thiophene (vide ante). Liquid 2,5-DHT was syringed at a rate of 0.12 ml/h (2.5×10^{-5} mol/min); D_2 flow was 31 ml/min (1.3×10^{-3} mol/min). The PbMo_6S_8 catalyst was heated to $400 \pm 1^\circ\text{C}$ in a stream of He (20 ml/min). The saturator, feedlines and valves were heated to $160 \pm 2^\circ\text{C}$ to ensure that 2,5-DHT (b.pt. = 122°C) was vaporized. Conversion of 2,5-DHT in the

empty reactor was negligible ($<0.5\%$). Reactor temperatures stabilized for 1 h before the reactor feed was brought on-line. Percent conversion of 2,5-DHT and the C_4 product distribution were monitored throughout the reaction. The products were trapped for mass and ^2H NMR spectral analyses over a period of 6 h.

2.6. Experiment C. Reaction of thiophene, D_2 and 2,5-DHT

A mixture of 2.5 ml (0.031 mol) of 2,5-DHT and 4.9 ml (0.062 mol) of thiophene was prepared; a 2.5 ml sample of it was loaded into the gas-tight syringe. The flow rate of this mixture was 0.12 ml/h; the D_2 flow was 31 ml/min (1.3×10^{-3} mol/min). The reactor was set up as for the reaction of 2,5-DHT with D_2 (vide ante). The products were monitored by GC. Trapping of the products at the vent was carried out for 6 h.

2.7. Experiment D. Reaction of 1,3-butadiene, D_2 and H_2S

The flow of butadiene was set at 0.048 ml/min (2.0×10^{-6} mol/min) as calibrated by GC; H_2S flow was set at either 0.043 ml/min (1.8×10^{-6} mol/min) or 0.74 ml/min (3.1×10^{-5} mol/min) using a bubble meter. The catalyst was heated to $400 \pm 1^\circ\text{C}$ in a He stream (20 ml/min), and the reactor system was allowed to stabilize for 1 h. The reactants were brought on-line in D_2 (31 ml/min, 1.3×10^{-3} mol/min), and the products were trapped at the vent. At the higher H_2S flow rate (0.74 ml/min, 3.1×10^{-5} mol/min), the reaction was run for 6 h; at the lower flow rate (0.043 ml/min, 1.8×10^{-6} mol/min), the reaction was run for 12 h. The C_4 product distributions were monitored throughout the reaction, and the products were trapped for analysis at the vent.

2.8. Experiment E. Reaction of thiophene, D_2 and 1,3-butadiene

The reactor was set up as above with the same flow rates of thiophene (0.12 ml/h, 2.5×10^{-5}

mol/min) and D_2 (31 ml/min, 1.3×10^{-3} mol/min). The catalyst was loaded to achieve 5% conversion of T; 1,3-butadiene was mixed with the reactant stream (0.18 ml/h, 7.5×10^{-6} mol/min). The C_4 product distribution was monitored throughout the reaction; the products were trapped at the vent for 12 h.

2.9. Deuterium analysis of 1,3-butadiene, thiophene and 2,5-DHT

For each reaction, the trapped products were vacuum transferred into a 5 mm NMR tube containing 0.50 ml CHCl_3 (distilled from CaH_2 under N_2) for analysis by ^2H NMR and mass spectrometry. The ^2H NMR spectra were obtained on a Varian VXR-300 spectrometer using CHCl_3 as the internal ^1H lock and standard ($\delta 7.24$ ppm). Mass spectral data for each component were obtained using a Finnigan 4000 GC-MS data system. The products were separated on a 30 m GS-alumina megabore (0.53 mm (i.d.), J and W Scientific) column. The deuterium contents of thiophene and butadiene (BDE) were determined from integrations of peaks corresponding to the parent ions (M) of these products containing different numbers of deuterium (D) atoms. Low ionization energy (13–16 eV) was used in the mass spectrometer in order to reduce the fragmentation of the parent ion. The $M-1$ peak (loss of H) was always less than 9%. All deuterium exchange data were corrected [21] by comparison to similar data for authentic, unreacted samples; this allowed for correction of naturally occurring ^2H , ^{13}C and ^{34}S and of the parent ion fragmentation. The resulting data were expressed as a deuterium distribution, d_0, d_1, \dots, d_n , where d_i is the fraction of the component containing i D atoms. This distribution can be represented as an average number of deuterium atoms per molecule, or deuterium number (D.N.) calculated using Eq. 2, where n is the total

$$\text{D.N.} = \sum_i^n i d_i \quad (2)$$

number of H atoms in the molecule. The total numbers of D atoms in each position on 1,3-buta-

diene (D_A , D_B , D_C , Fig. 1) were calculated using equation 3 where i is the D_A , D_B , or D_C

$$D_i = \left(\frac{I_i}{\sum I_i} \right) \text{D.N.} \quad (3)$$

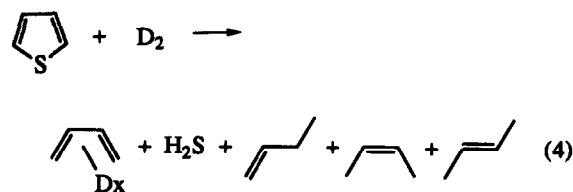
position, and I_i is the integral of the corresponding peaks in the ^2H NMR spectrum.

3. Experimental results

3.1. Deuterodesulfurization of thiophene.

Experiment A (Eq. 4)

Product distributions for reactions of thiophene at $400 \pm 1^\circ\text{C}$ under steady state conditions with deuterium gas (Eq. 4) at five different catalyst loadings of PbMo_6S_8 are shown in Table 2.



No hydrogenated thiophenes (2,3-DHT, 2,5-DHT or THT), butanethiol or butane were detected under these conditions. The catalyst loading was varied to produce different levels of thiophene

Table 2

Conversion and product distribution from thiophene deuterodesulfurization over PbMo_6S_8 at 400°C (Experiment A) ^a

	Reaction number				
	1	2	3	5	6
g PbMo_6S_8	0.403	0.327	0.195	0.126	0.110
space time (g min/ml)	0.013	0.011	0.0063	0.0041	0.0035
Conversion (%)					
Thiophene	89.8	91.9	93.2	97.4	99.1
C_4 's	10.2	8.09	6.81	2.63	0.86
C_4 Product distribution (%)					
1-Butene	47.7	52.0	53.3	67.7	70.8
<i>cis</i> -2-Butene	22.0	19.4	19.2	10.7	trace
<i>trans</i> -2-Butene	26.7	23.9	21.9	11.5	trace
1,3-Butadiene	3.50	4.67	5.65	10.1	29.2

^a Thiophene flow rate was 0.12 ml/h (2.5×10^{-5} mol/min); D_2 flow rate was 31 ml/min (1.3×10^{-3} mol/min).

conversion to C_4 products. The relative amounts of *cis*- and *trans*-2-butenes decrease as thiophene conversion decreases, with only trace amounts ($<0.5\%$) detected at the lowest conversion (0.86%). On the other hand, the relative amounts of 1-butene and BDE increase as conversion decreases; the increase in BDE is consistent with it being the initial product of HDS. The amount of 1-butene is always in excess of the equilibrium distribution at 400°C (equilibrium at 400°C : 20% 1-butene, 49% *trans*-2-butene; 31% *cis*-2-butene) [5], which is consistent with it being formed as the initial product of BDE hydrogenation. It is unlikely that 1-butene is the initial product which dehydrogenates to butadiene under the D_2 atmosphere. This is supported by the observation that 1-butene, when passed over PbMo_6S_8 at 400°C , produces no BDE [6].

Deuterium distributions in the unreacted thiophene and BDE products at different catalyst loadings are shown in Table 3. The reaction run numbers in Table 3 correspond to those in Table 2. Thiophene deuterium numbers (D.N.) decrease (0.42–0.05) with decreasing thiophene conversion (10.2–0.86%). A plot (Fig. 7) of thiophene D.N. against thiophene conversion is nearly linear, as would be expected from the decreased residence time in the catalyst bed. Thus, the amount of deuterium exchange on thiophene is dependent on the amount of conversion.

The sites (Fig. 1) of deuterium exchange in thiophene and BDE can be determined by integrating peaks in the ^2H NMR spectrum. A typical ^2H NMR spectrum of the olefinic region is shown in Fig. 8. The peaks are slightly broadened as compared to an ^1H NMR spectrum due to quadrupolar relaxation of the nuclei; however, the chemical shifts (in ppm) are essentially the same in the ^1H and ^2H NMR spectra of butadiene and butadiene- d_6 [22,23]. Coupling constants between two ^2H atoms is usually only 2.3% of the corresponding coupling between two ^1H atoms; coupling between ^1H and ^2H is about 15% of the corresponding ^1H , ^1H coupling. Thus, ^1H , ^2H coupling most likely accounts for the observed splittings in the ^2H NMR spectrum (Fig. 8). The peaks

Table 3

Deuterium distribution and deuteration sites in 1,3-butadiene and thiophene produced during thiophene deuterodesulfurization over PbMo_6S_8 at 400°C (Experiment A) ^a

	Reaction number				
	1	2	3	4	5
Deuterium distribution in BDE					
d_0	0.0077	0.0100	0.0110	0.0177	0.0255
d_1	0.0573	0.0586	0.0616	0.0255	0.0491
d_2	0.172	0.159	0.147	0.121	0.176
d_3	0.297	0.298	0.300	0.254	0.301
d_4	0.252	0.264	0.261	0.278	0.275
d_5	0.158	0.157	0.165	0.227	0.145
d_6	0.0553	0.0545	0.0542	0.0775	0.0290
BDE D.N.	3.42	3.44	3.45	3.74	3.30
Deuterium location (see Fig. 1) in BDE					
D_A	0.79	0.78	0.86	0.91	0.85
D_B	1.41	1.36	1.36	1.40	1.19
D_C	1.23	1.31	1.23	1.44	1.26
A:B:C	1:1.8:1.6	1:1.8:1.7	1:1.6:1.4	1:1.5:1.6	1:1.4:1.5
Deuterium content in T					
Thiophene D.N.	0.42	0.29	0.23	0.08	0.05

^a See footnote a in Table 2 for reactant amounts and conditions.

for thiophene (E, δ 7.40 ppm (s) and G, δ 7.19 ppm (s) in Fig. 2) indicate that most of the deuterium exchange (95%) occurs in the 2- and 5-positions rather than the 3,4-positions; predominant exchange in the 2,5-positions has also been observed over MoS_2 and $\text{Co-Mo}/\text{Al}_2\text{O}_3$ [24,25].

Deuterium numbers calculated from the mass spectral data (eq 2) for BDE remain constant (average D.N. = 3.47) despite the decrease in thiophene conversion (Table 3, Fig. 7) from 10.2% to 0.86%. The mass spectrometric data (Table 3) indicate that the BDE deuterium content ranges from d_0 to d_6 ; butadiene- d_3 and butadiene- d_4 are the major BDE products.

The amount of deuterium in each position (D_A , D_B , D_C ; Table 3) was calculated from the D.N. and integrals of the individual peaks in the ^2H NMR spectra (Eq. 3). Peaks for butadiene (D_A , δ 6.38 ppm (s); D_B , δ 5.25 ppm (m); D_C , δ 5.14 ppm (m); Fig. 8) in the ^2H NMR spectra are easily distinguished from those of 1-butene (H, δ 5.90 (s) and 4.99 ppm (d)) and the 2-butenes (I, δ 5.47 ppm (d)) which allows the D_A , D_B and D_C butadiene peaks to be integrated. The amount of

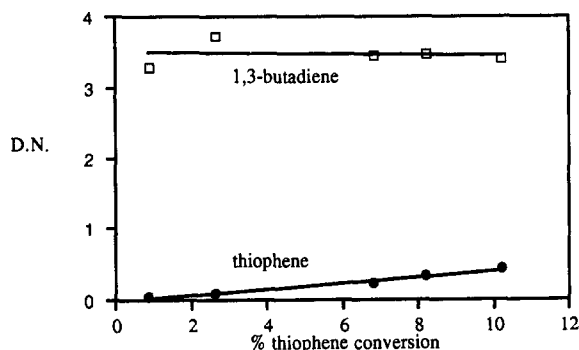
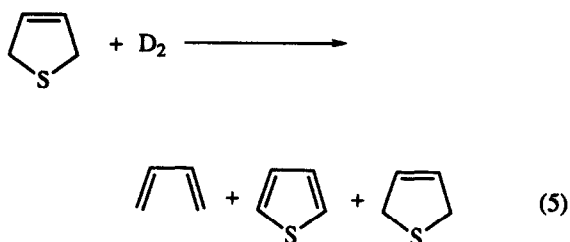


Fig. 7. Change in thiophene D.N. and 1,3-butadiene D.N. with % thiophene conversion (Experiment A, Eq. 4).

deuterium in the D_A position (0.78–0.91) (Table 3) is always less than that in either the D_B (1.19–1.41) or D_C (1.23–1.44) positions.

3.2. DDS of 2,5-DHT. Experiments B and C (Eq. 5)

Product distributions for the reaction of 2,5-DHT with D_2 (Experiment B) (Eq. 5) and for the mixture of thiophene and 2,5-DHT with D_2 (Experiment C) are shown in Table 4. The reaction of



2,5-DHT with D_2 produces 27.7% BDE as the only desulfurized product; butenes are present in trace amounts ($<1\%$). The dehydrogenated product thiophene is also detected. Thiophene was also detected from 2,5-DHT HDS over 5% Re/ Al_2O_3 at $400^\circ C$ (7c). Although the amount of thiophene decreases from 52% at the beginning of the run to 15% after 6 h and the amount of unreacted 2,5-DHT increases from 25% to 61%

during the same time, the amount of BDE remains constant. The 1,3-butadiene also incorporates virtually no deuterium (99% is d_0 and d_1 , D.N. = 0.04) as does thiophene (D.N. = 0.04) for samples collected over the 6 h duration of the run (Table 5); 2,5-DHT is all d_0 . Although the amounts of thiophene and 2,5-DHT change during the run, there is no effect of this change on the incorporation of deuterium into butadiene or 2,5-DHT.

When thiophene is added to 2,5-DHT (Experiment C) in a 2:1 mole ratio, the conversion to C_4 products drops to 20.5% (Table 4), 91% of which is 1,3-butadiene. Small amounts of 1-butene (4.7%), *cis*-2-butene (1.9%) and *trans*-2-butene (2.2%) are also detected; again 1-butene is in excess of the equilibrium distribution of butenes. At the beginning of the reaction, all of the 2,5-

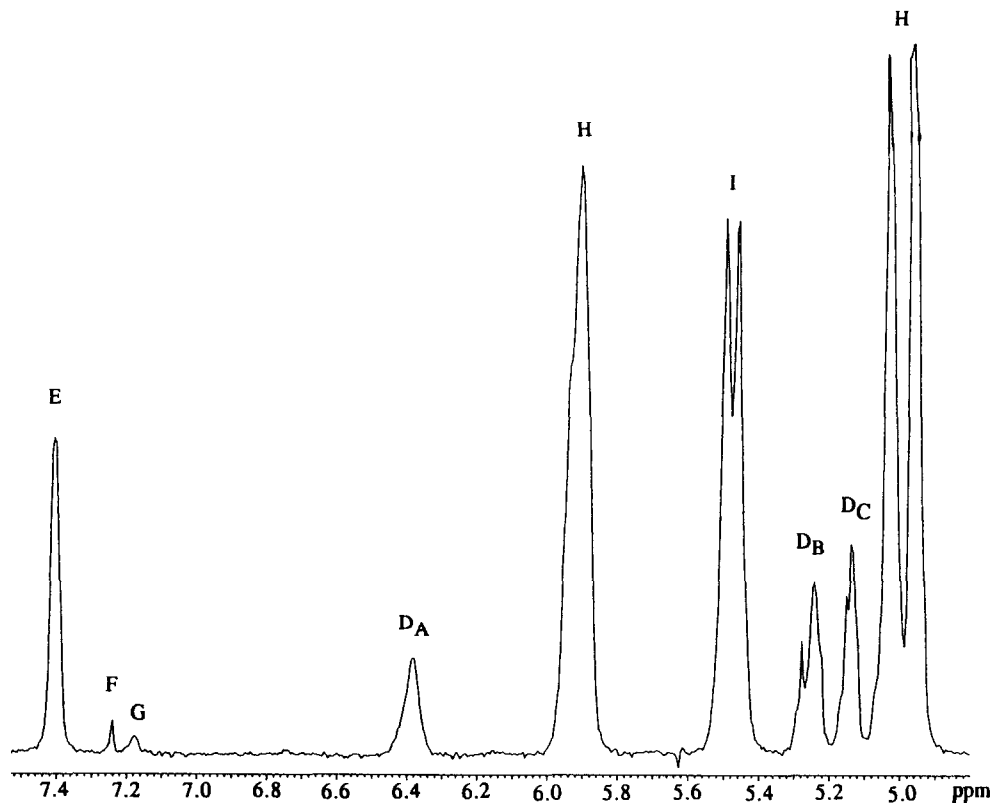


Fig. 8. Olefinic region of an 2H NMR spectrum of DDS reaction products. Labeled peaks are as follows: D_A , D_B and D_C of 1,3-butadiene (BDE) with labeled positions corresponding to those in Fig. 1; E is the 2,5-positions on thiophene; F is $CDCl_3$ in $CHCl_3$ solvent; G is the 3,4-position on thiophene; H is 1-butene; I is 2-butenes.

Table 4

Product distributions from reactions of D₂ with 2,5-DHT (Experiment B), 2,5-DHT and thiophene (Experiment C), and H₂S and 1,3-butadiene (Experiment D) over PbMo₆S₈ at 400°C^a

	Experiments			
	B ^b	C ^c	D ^d	D ^e
Conversion (%)				
2,5-DHT	25 ^f –61 ^g	0 ^f –8.3 ^g	–	–
T	52 ^f –15 ^g	73 ^f –79 ^g	–	–
C ₄ 's	27.7	20.5	100	100
C ₄ Product distribution (%)				
1-Butene	< 1%	4.7	30.71	6.70
cis-2-Butene	trace	1.9	22.66	5.23
trans-2-Butene	trace	2.2	24.39	5.71
Butadiene	≈ 99	≈ 91	32.24	82.36

^a D₂ flow was 31 ml/min (1.3 × 10⁻³ mol/min) for all reactions; 0.20–0.21 g of catalyst used in all reactions.

^b 2,5-DHT flow rate was 0.12 ml/h (2.5 × 10⁻⁵ mol/min).

^c 2:1 mole ratio of thiophene (0.08 ml/h, 1.7 × 10⁻⁵ mol/min) and 2,5-DHT (0.04 ml/h, 8.3 × 10⁻⁶ mol/min) in the feed.

^d Low H₂S flow of 0.043 ml/min (1.8 × 10⁻⁶ mol/min) and BDE flow of 0.048 ml/min (2.0 × 10⁻⁶ mol/min).

^e High H₂S flow of 0.74 ml/min (3.1 × 10⁻⁵ mol/min) and BDE flow of 0.048 ml/min (2.0 × 10⁻⁶ mol/min).

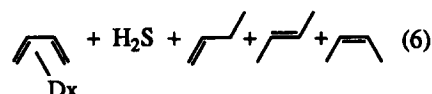
^f Start of reaction.

^g After 6 h of continuous reaction.

DHT is converted to either C₄ products or thiophenes; however, after 3 h, 2,5-DHT is detected and its concentration steadily increases to 8% after 6 h. Virtually no deuterium (Table 5) is incorporated into either 2,5-DHT (D.N. = 0.0) or thiophene (D.N. = 0.02), but the amount of deuterium in BDE (D.N. = 0.33) is greater than it was in the reaction (Experiment B) of just 2,5-DHT with D₂. The deuterium in the BDE obtained from the 2,5-DHT, thiophene, D₂ reaction may come at least in part from the BDE produced from thiophene DDS. The ratio of deuterium in the D_A, D_B and D_C positions in BDE is the same as that obtained from thiophene DDS (Table 3).

3.3. Reaction of 1,3-butadiene, H₂S and D₂. Experiment D (Eq. 6)

The BDE flow rate was set (0.048 ml/min, 2.0 × 10⁻⁶ mol/min) at a level corresponding



to the amount of C₄ products observed at 10% thiophene conversion (Experiment A). In separate reactions, the flow of H₂S was set at a level corresponding to the equivalent amount of thiophene (0.74 ml/min, 3.1 × 10⁻⁵ mol/min) and at the amount corresponding to the H₂S produced during thiophene HDS (0.043 ml/min, 1.8 × 10⁻⁶ mol/min). The H₂S and BDE were passed over the catalyst together with D₂ gas at a

Table 5

Deuterium distribution in 1,3-butadiene and thiophene produced in reactions of D₂ with 2,5-DHT (Experiment B), 2,5-DHT and thiophene (Experiment C), H₂S and 1,3-butadiene (Experiments D), and thiophene and 1,3-butadiene (Experiment E)^a

	Experiment				
	B ^b	C ^c	D ^d	D ^e	E ^f
Deuterium distribution in BDE					
d ₀	0.974	0.792	0.124	0.992	0.187
d ₁	0.019	0.130	0.157	0.008	0.270
d ₂	0.004	0.044	0.221	–	0.285
d ₃	0.002	0.024	0.229	–	0.146
d ₄	–	0.009	0.165	–	0.078
d ₅	–	0.001	0.082	–	0.029
d ₆	–	–	0.022	–	0.005
BDE D.N.	0.04	0.33	2.49	0.01	1.58
Deuterium location (see Fig. 1) in BDE					
D _A	0.01	0.09	0.53	– ^g	0.29
D _B	0.02	0.13	1.04	–	0.64
D _C	0.01	0.12	0.91	–	0.65
Deuterium content in 2,5-DHT and T					
2,5-DHT D.N.	0.0	0.0	–	–	–
Thiophene D.N.	0.04	0.02	–	–	0.08

^a D₂ flow for all reactions was 31 ml/min (1.3 × 10⁻³ mol/min) over PbMo₆S₈ at 400°C.

^b 2,5-DHT flow rate was 0.12 ml/h (2.5 × 10⁻⁵ mol/min).

^c 2:1 mole ratio of thiophene (0.08 ml/h, 1.7 × 10⁻⁵ mol/min) and 2,5-DHT (0.04 ml/h, 8.3 × 10⁻⁶ mol/min) in the feed.

^d Low H₂S flow 0.043 ml/min (1.8 × 10⁻⁶ mol/min) and BDE flow of 0.048 ml/min (2.0 × 10⁻⁶ mol/min).

^e High H₂S flow 0.74 ml/min (3.1 × 10⁻⁵ mol/min) and BDE flow of 0.048 ml/min (2.0 × 10⁻⁶ mol/min).

^f Thiophene flow of 0.12 ml/min (2.5 × 10⁻⁵ mol/min) and BDE flow of 0.18 ml/min (7.5 × 10⁻⁶ mol/min).

^g No BDE was detected in ²H NMR.

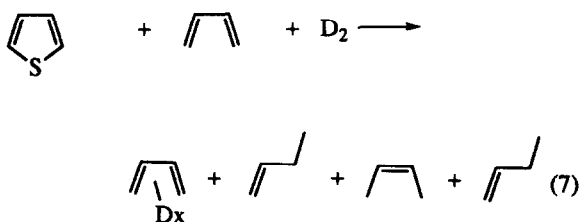
flow rate of 31 ml/min (1.3×10^{-3} mol/min). The C_4 product distributions are shown in Table 4. At both H_2S flow rates, the C_4 product distribution remained constant for the entire reaction (6 h and 12 h) indicating steady state conditions were achieved. The effect of catalyst poisoning by H_2S is seen in the product distributions; at the lower H_2S flow rate, 68% of the BDE is hydrogenated compared to only 18% at the higher H_2S flow rate. In both cases, 1-butene is in excess of the equilibrium values for butenes at 400°C [5].

The deuterium content in BDE from the reactions of H_2S , BDE and D_2 (Table 5) is reduced by the presence of H_2S . At the lower H_2S flow (0.043 ml/min, 1.8×10^{-6} mol/min), the D.N. is 2.49 (90% d_0 - d_4), indicating that butadiene undergoes significant exchange over the HDS catalyst. However, at the higher H_2S flow (0.74 ml/min, 3.1×10^{-5} mol/min) where the number of moles of H_2S feed is similar to that of thiophene in thiophene DDS (Experiment A) (2.5×10^{-5} mol/min of thiophene), 99% of the butadiene does not undergo deuterium exchange (D.N. = 0.01). Since the amount of H_2S produced in the DDS of thiophene is similar to that in the low-level H_2S experiment, it seems likely that the formed D_2S (or H_2S) in the DDS of T will not completely inhibit deuterium exchange with the butadiene that is formed. However, the large excess of thiophene may be sufficient to essentially prevent this exchange as suggested by other experiments.

3.4. Reaction of thiophene, BDE and D_2 .

Reaction E (Eq. 7)

The flow rate of BDE (0.18 ml/min, 7.6×10^{-6} mol/min) was set at approximately six



times the amount of C_4 products produced during thiophene DDS (Experiment A, Eq. 4) at 5% thiophene conversion. Thus, the majority of BDE trapped and analyzed should be from the added BDE and not a product of thiophene DDS. Without thiophene in the feed stream, but otherwise using the same conditions, BDE is completely hydrogenated to 1-butene and *cis*- and *trans*-2-butenes at 400°C over $PbMo_6S_8$. No butane is detected. A small amount of cracking (5%) to C_3 and C_2 products is also observed. Thus, thiophene in the reactant feed inhibits BDE hydrogenation. This reaction (Eq. 7), however, does not achieve steady state conditions. Fig. 9 shows a dramatic change in C_4 product distribution during the 12 h reaction. The relative amount of 1-butene stays constant; BDE increases while *cis*- and *trans*-2-butene decrease. There is always an excess of 1-butene over the equilibrium value for the 1- and 2-butenes at 400°C [5]. The D.N. of BDE is significantly less (1.58) (Table 5) than that of BDE from thiophene DDS. Only 0.29 D atoms (Eq. 3) are in the D_A -position, indicating that most of the deuterium exchanges into the D_B - and D_C -positions. Since the reaction does not achieve a steady state, the catalyst is changing during the course of the reaction, and the results cannot be compared with data from the other reactions that are obtained under steady-state conditions.

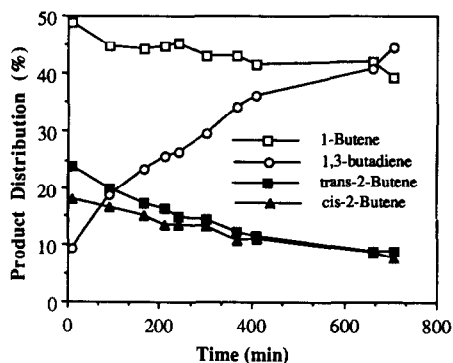


Fig. 9. Change in product distribution with time for the reaction of thiophene, 1,3-butadiene (BDE) and D_2 over $PbMo_6S_8$ at 400°C (Experiment E, Eq. 7).

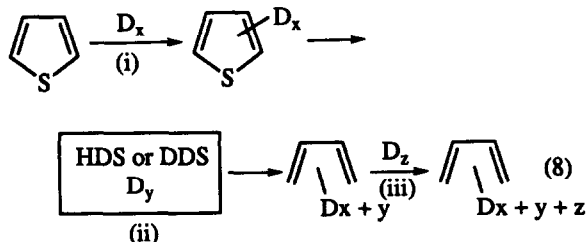
4. Discussion of results

4.1. 1,3-Butadiene as the initial HDS product

The results of our study of thiophene DDS (Experiment A, Eq. 4) indicate that BDE is the first desulfurized product, which is subsequently hydrogenated to give the observed C₄ product distribution. This conclusion is supported by the following discussion. First, the relative amount of butadiene (Table 2) increases with decreasing thiophene conversion. This same trend, indicative of a sequential pathway, has been observed over other Chevrel phase catalysts [4] and over MoS₂ [3a]. Second, the 1-butene produced during the reaction (Table 2) is always in excess of the equilibrium distribution of butenes [5] at 400°C; 1-butene is also in excess during the hydrogenation of BDE in a BDE and H₂S mixture (Experiment D) and over MoS₂ [26]. Third, hydrogenation of 1-butene over PbMo₆S₈ and other Chevrel phase catalysts [6a] does not produce BDE. Thus, the evidence supports the conclusion that the BDE produced in our reactions (Experiment A) is the first product of thiophene DDS.

4.2. Deuterium content in 1,3-butadiene

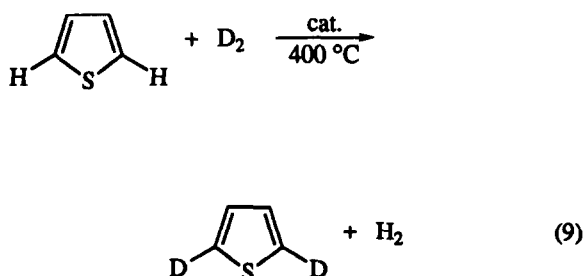
The deuterium observed experimentally in BDE formed during thiophene DDS could be incorporated at any of three stages of the reaction (Eq. 8): in stage (i), thiophene itself could exchange to incorporate *x* deuterium atoms; in stage (ii), the thiophene



undergoes HDS to give BDE, which must incorporate at least two deuteriums in order to be formed but could contain a total of *y* deuterium atoms; in stage (iii), the formed BDE may

undergo exchange to incorporate *z* deuterium atoms. So the total deuterium content in the final BDE is the sum (*x* + *y* + *z*) gained in each of the three stages. We sought to determine the amount of deuterium (D_y) incorporated in only the DDS stage (ii) of the reaction. In order to establish D_y, the number of deuteriums gained during just the DDS portion of the process (stage ii), it is necessary to determine D_x and D_z in stages (i) and (iii); D_x and D_z are discussed below.

It is entirely possible that deuterium incorporation will occur in stage (i) as thiophene is known to undergo deuterium exchange (Eq. 9), primarily into the α-position, over a variety of



HDS catalysts [24,25], including PbMo₆S₈ [4]. In this study, D exchange of the α-protons on thiophene during DDS varies with the amount of thiophene conversion (Experiment A, Tables 2 and 3, Fig. 7). At the highest conversion of 10.2%, the D.N. is equal to 0.42; this drops to 0.05 at the lowest conversion (0.86%). Thus, deuterium incorporation in stage (i) is relatively small with D_x ranging from D_{0.4} to D_{0.1} or less, and almost all of this deuterium would appear in the D_B and D_C positions (Fig. 1) of the BDE product.

Our results indicate that in stage (iii) (Eq. 8) the BDE does not undergo deuterium exchange; thus, D_z is D₀. The lack of deuterium exchange in the formed BDE appears to result from H₂S/thiophene deactivation of the exchange sites. These conclusions are supported by the following results. (a) At different levels of thiophene conversion, the deuterium content (D.N. = 3.47) of BDE remains virtually constant (Tables 2 and 3, Fig. 7). If deuterium were exchanging with the formed BDE, a decrease in D.N. with decreasing

thiophene conversion would be expected. Deuterium exchange of thiophene itself shows this trend (Fig. 7). (b) Butadiene can be formed in situ by passing 2,5-DHT with D_2 over the $PbMo_6S_8$ catalyst. This is also known to occur in reactions of 2,5-DHT with H_2 over 5% Re/Al_2O_3 [7]; in addition, BDE is liberated when 2,5-DHT adsorbs to a Mo(110) single crystal surface [27], and organometallic complexes containing 2,5-DHT as a ligand [7,28] liberate BDE when heated. In the present studies, 2,5-DHT (0.12 ml/h , $2.5 \times 10^{-5}\text{ mol/min}$) when passed with D_2 over $PbMo_6S_8$ gives BDE as the only C_4 hydrocarbon product (Experiment B, Table 4). The BDE formed is 97.4% d_0 (D.N. = 0.04, Table 5) indicating that the BDE does not exchange significantly with deuterium under these conditions. Similar results were obtained for the DDS of 2,5-DHT over 5% Re/Al_2O_3 at 300°C , where BDE incorporated slightly more deuterium (D.N. = 0.51) [7]. When thiophene, 2,5-DHT and D_2 were reacted (Experiment C, Tables 4, 5), the resulting BDE contains more deuterium (D.N. = 0.33) than that obtained from only 2,5-DHT and D_2 (DN = 0.04). The higher BDE deuterium content in this reaction (Experiment C) appears to result from the BDE produced in the DDS of thiophene. Assuming 5% conversion of thiophene (based on the amount of catalyst), this reaction was run with 10 equivalents of 2,5-DHT for every mole of BDE produced from thiophene. The BDE D.N. of 0.33 is 1/10 of that produced from just thiophene DDS, and the $D_A:D_B:D_C$ ratios are similar to those in BDE produced in the DDS of thiophene (Experiment A). This suggests that deuterium is incorporated only into BDE from thiophene DDS, not from 2,5-DHT DDS. (c) H_2S inhibits both the hydrogenation and the deuterium exchange (Experiment D, Tables 4, 5) of BDE over this catalyst. Complete hydrogenation of BDE to butenes is observed over $PbMo_6S_8$ at 400°C ; however, when H_2S ($3.1 \times 10^{-5}\text{ mol/min}$) is added to the feed at a level similar to that of thiophene ($2.5 \times 10^{-5}\text{ mol/min}$) and the butadiene flow ($2.0 \times 10^{-6}\text{ mol/min}$) is similar to that of the C_4 products obtained from 10% thiophene conversion, 82% of

the 1,3-butadiene passes through unhydrogenated and unexchanged (99% d_0). Results from static reactor studies of BDE and D_2 over MoS_2 [26] and mixtures of D_2S and BDE over MoS_2 [26] also indicate that BDE does not undergo exchange. In these MoS_2 studies, greater than 94% of the BDE did not exchange. Thus, the above studies indicate that once BDE is formed from thiophene, it is either hydrogenated to 1-butene, or it passes through the catalyst without undergoing exchange. This is not unreasonable as BDE is very active toward hydrogenation, such that, once in contact with an active site, hydrogenation of BDE is faster than deuterium exchange. Thiophene, H_2S and 2,5-DHT all poison the catalyst, inhibiting both the hydrogenation and deuterium exchange of butadiene under these conditions.

4.3. The HDS mechanism

Based on the above discussion, we can estimate that of the 3.47 D atoms found in the BDE resulting from the DDS of thiophene over $PbMo_6S_8$ at 400°C , 0.05–0.42 D are introduced in stage (i) (Eq. 8); this exchange of D into thiophenes before DDS occurs will introduce 0.05–0.4 D into the D_B and D_C positions of the 1,3-butadiene product. Using a value of 0.3 D for stage (i), this means that of the total 3.47 D observed in the BDE, 3.2 D are introduced in the HDS step, stage (ii), of the reaction. Of these 3.2 deuteriums, 0.83 D are in the D_A -position and approximately 1.2 D are in each of the D_B and D_C positions. Any mechanism for HDS must account for this number and the distribution of deuterium atoms in the BDE, but it must also account for the fact that there is considerable exchange of deuterium atoms during HDS (stage ii) that accounts for butadiene with D content ranging from d_0 (1.2%) to d_6 (5.5%) but mostly d_3 (28%) and d_4 (27%) (Table 3). All of the mechanisms discussed in the Introduction and summarized in Table 1 involve processes that give specific numbers of deuteriums in specific positions; none accounts for the formation of d_0 or d_6 , for example. Although some of these species are formed in low amounts, there must be

an exchange step in the HDS process that allows their formation. Since the exchange is likely to involve surface deuterium atoms, any exchange will likely *add* deuteriums to the number introduced by the DDS process itself. Thus, of the 3.2 deuteriums introduced in stage (ii) most were probably added during the DDS process, but some may have been added by scrambling. Any mechanisms that produce BDE with *more than 3.2 D* are inconsistent with the results. This eliminates the mechanisms (Table 1) in Figs. 4 and 5 as pathways for thiophene HDS over this catalyst (PbMo_6S_8) under these conditions. Both of these mechanisms are also inconsistent with the number of deuteriums at the D_A position, since they both predict 1.5–2.0 D in this position, whereas only 0.83 D are observed.

The mechanism in Fig. 3 proposed by Kwart, Schuit and Gates [10] is possibly consistent with our results depending on which pathway (steps *c*, *d*, *f*, *g* and *h* or steps *e*, *f* and *i*) predominates (Table 1). The first pathway (steps *c*, *d*, *f*, *g* and *h*) introduces as many as 3.5 D atoms into BDE with up to 1.5 D atoms in the D_A -position, if one assumes a deuterium isotope effect [9]. This mechanism would not be consistent with the experimental results as more than 3.2 D are predicted for BDE with more than 0.83 D in the A -position. However, the latter pathway (steps *e*, *f* and *i*) leads to 2.0 D atoms incorporated in the D_B - and D_C -positions of BDE; thus, this mechanism is consistent with our results if a separate exchange process is included. Also, if both pathways are involved, they may together account for the observed amount of deuterium in BDE, the amount of deuterium in the D_A -position, as well as provide a mechanism for the exchange seen in d_2 – d_4 ; yet it still does not account for butadiene- d_0 , $-d_1$, $-d_5$ and $-d_6$.

The mechanisms in Figs. 2 and 6 are also consistent with the BDE deuterium results. Since the mechanism in Fig. 2 [7] introduces a maximum of 2.8 D atoms during the HDS process, the additional 0.4 D atoms must be added during a separate exchange step. That this can occur is supported by the observation [7] that the DDS of 2,3-

DHT (product of step (*b*) in Fig. 2) over 5% Re/ Al_2O_3 at 300°C introduces 1.20 D atoms, mainly at the olefinic positions, into the unconverted 2,3-DHT; the BDE produced from this reaction contains 4.06 D atoms. Thus 2,3-DHT is an intermediate that may account for the extra D incorporation and the exchange of D atoms which results in the d_0 – d_6 distribution in the BDE. It is unlikely however, that deuterium exchange occurs in the 2,5-DHT intermediate (product of step (*c*)) since the BDE produced in the DDS of 2,5-DHT over PbMo_6S_8 (Table 4, Experiments B and C) is 97% d_0 , and 2,5-DHT incorporates no deuterium.

Another mechanism that is consistent with the results of this work is shown in Fig. 6 [14]. The mechanism itself accounts for the incorporation of only two deuterium atoms (Table 1) into BDE (step *f*). Deuterium exchange with one or more of the intermediates in this mechanism would account for the incorporation of D atoms in the D_A -position and the d_0 – d_6 distribution. In this case, however, there are no reported studies of D exchange with the intermediates. The other mechanisms [15–18] which result in the addition of two D atoms to the D_B - and D_C -positions are also consistent with the results of this study for the same reasons.

5. Conclusion

The results of this study indicate that a mechanism for thiophene HDS over PbMo_6S_8 must account for a maximum of 3.2 deuterium atoms being incorporated into 1,3-butadiene including 0.83 D in the D_A -position and 1.2 D atoms in each of the D_B - and D_C -positions. Two mechanisms (Figs. 4, 5) can be ruled out as they predict more deuterium per butadiene molecule than is found in these studies. Other mechanisms (Figs. 2, 3 and 6) which predict fewer than 3.2 deuteriums in each 1,3-butadiene molecule, are consistent with the results of this study, assuming that there is an exchange step which increases the overall deuterium content and yields the observed d_0 – d_6 distribution of deuterated butadiene. It should be

emphasized that these conclusions apply to the PbMo_5S_8 -catalyzed reaction; mechanism(s) for thiophene HDS on $\text{CoMo}/\text{Al}_2\text{O}_3$ or other catalysts may or may not be same.

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