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Deuterium Exchange of Benzo[b]thiophene: Model Complex and Heterogeneous Reactor Studies

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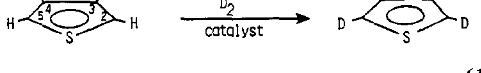
The complexes $[CpRu(BT)]^+$ and $[CpRu(3\text{-}MeBT)]^+$, where BT is benzo[b]thiophene and 3-MeBT is its 3-methyl derivative, are models for π-coordination of BT to hydrodesulfurization (HDS) catalysts via the benzene ring. The BT in these complexes undergoes base-catalyzed deuterium exchange, at the 2 and 7 positions; in KOH/CD_3OD solutions, the exchange follows the rate law: rate = k[Ru complex][OH^-]. The mechanism is proposed to involve rate-determining proton abstraction by OH^- from either $[CpRu(BT)]^+$ or $[CpRu(3\text{-}MeBT)]^+$ followed by transfer of D^+ from the CD_3OD solvent to give the deuterated BT complex. Heterogeneous reactor studies of deuterium exchange of BT with D_2 over several HDS catalysts ($PbMo_{6.2}S_8$, $Co_{0.25}MoS$, and 5% Re/γ-Al_2O_3) and γ-Al_2O_3 indicate that BT is activated to exchange at the 2 and 3 positions over the catalysts. These results suggest that deuterium exchange of BT over HDS catalysts may occur through routes other than those involving BT π-bonding through its benzene ring to the catalyst surface.

INTRODUCTION

The industrial importance of the process of catalytic hydrodesulfurization (HDS), generally accomplished using a cobalt-promoted molybdenum catalyst and resulting in the removal of sulfur from organosulfur compounds found in crude oils and coal liquids (*1*), is widely recognized (*2*). Because of the extensive application of HDS, numerous investigations aimed at obtaining a better understanding of the process have been undertaken (*3*). However, the mode of coordination of the sulfur compounds to the catalyst surface as well as key steps of the desulfurization is still not well understood.

Since the study of deuterium exchange reactions provides an opportunity for learning about the nature and reactivity of adsorbed intermediates on catalyst surfaces (*4*), several deuterium exchange investigations of representative sulfur-containing compounds over HDS catalysts have been reported (*5*). The compound usually chosen is thiophene (T) (*5, 6*) which is the simplest member of the largest class of organosulfur compounds found in crude oils (*7*). The exchange occurs most readily in the 2 and 5 positions, as shown in Eq. (1), with lesser amounts of exchange occurring in the 3 and 4 positions,



(1)

The exchange of methyl derivatives of T has also been investigated (*6b,e*). The results of these studies have been interpreted as supporting various adsorption modes, reaction pathways, and types of catalytic sites present on the surface. Recently, the rates of deuterium exchange in

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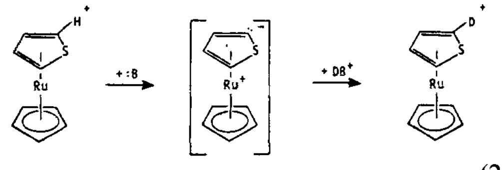
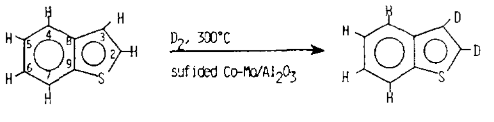
the π-thiophene ligands of $[CpRuL]^+$ (L = T, 2-MeT, 3-MeT, 2,3-Me_2T), as models of π-adsorbed thiophenes on HDS catalysts, have been reported (*8*). The rate-determining step of the exchange reaction, shown for the T complex in Eq. (2), was proposed to be H^+ abstraction from T by OH^-,



(2)

The deuterated compound is then produced by D^+ transfer from the CD_3OD solvent (*8a*). The rates of exchange for the different hydrogens in the complexes ($H_{2,5} > H_{3,4} > CH_3$) follow the same order as the relative amounts of deuterium exchanged into these positions over HDS catalysts. These results provide support for the proposal that π-adsorbed thiophenes (T's) are intermediates in the deuterium exchange of T's on catalyst surfaces.

Although the mechanism of T HDS has been intensively investigated, it has been suggested that benzo[b]thiophene (BT) and its derivatives would actually provide better models for studies of the HDS process (*9*). In addition to their being more difficult to desulfurize than T, they are usually the predominant type of thiophenic compound found in crude oils and coal liquids (*10, 11*). A number of reports of BT HDS reactor studies have appeared (*3, 7, 11, 12*), but only one addresses the deuterium exchange reaction of BT (*6c*). Cowley interpreted ^1H and ^2H NMR spectra as well as mass spectral fragmentation data of the deuterated BT to indicate that BT undergoes preferential exchange at the 2 and 3 positions of BT as shown in



(3)

He concluded that this result supported, π-coordination of the thiophene ring of BT to the catalyst surface because a one-point sulfur coordination mode would give rise to exchange at the 2 and 7 positions. Flat, π-coordination of BT to HDS catalysts has been proposed by others (*12a, 13*).

Our approach to understanding how π-adsorbed BT might react on HDS catalysts is to study π-bound BT's in transition metal model complexes (*14*). In this paper, the base-catalyzed deuterium exchange reactions of $[CpRu(BT)]PF_6$, **1**, and $[CpRu(3\text{-}MeBT)]PF_6$, **2**, are reported. Because Cowley's experiments were conducted using a 60-MHz NMR instrument, which was not capable of resolving either the H4 and H7 or the H2, H3, H5, and H6 resonances of BT, we also reexamined the exchange reactions of BT over HDS catalysts. By using a 300-MHz NMR instrument, all of the resonances of BT except H5 and H6 are resolved (Fig. 1) and, therefore, the positions at which exchange occurs can be clearly established. The results of studies which employed a variety of catalysts ($PbMo_{6.2}S_8$, $Co_{0.25}MoS$, and 5% Re/γ-Al_2O_3), as well as γ-Al_2O_3, are presented.

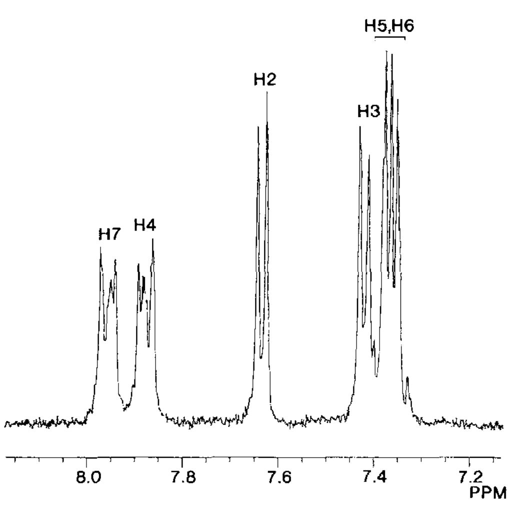


FIG. 1. ^1H NMR spectrum (300 MHz) of benzo[b]thiophene in acetone-d_6

EXPERIMENTAL

General Procedures

The compounds [CpRu(BT)]PF_6 (*14*), **1**, [CpRu(3-MeBT)]PF_6 (*14*), **2**, and [CpRu(η-C_6H_6)]PF_6 (*15*) were prepared by literature methods. The CD_3OD (99.5%) was purchased from Cambridge Isotope Laboratories and stored over 4-Å molecular sieves under N_2. The BT and 0.5 *N* KOH/CH_3OH solution were purchased from Aldrich. The ^1H NMR spectra were obtained on a Nicolet NT-300 spectrometer using deuterated solvents as internal locks and the ^2H NMR spectra were obtained on a Bruker WM-300 spectrometer using acetone as an internal lock.

Preparation of Samples, Data Collection, and Analysis of the Kinetic Data

The 0.10–1.1 *M* concentrations of KOH/CD_3OD solutions were obtained as follows. The required amount of the standard KOH/CH_3OH solution was measured using a 1.00-ml syringe and added to a 5-mm NMR tube which was then capped with a rubber septum. The CH_3OH solvent was removed *in vacuo*. Then, 0.30 ml of CD_3OD was added to the NMR tube which was recapped and shaken to dissolve the KOH. At this point either **1** (0.0046 g, 1.0×10^{-5} mol, 0.033 *M*) or **2** (0.0048 g, 1.0×10^{-5} mol, 0.033 *M*) was added to the NMR tube. The septum was then sealed with Parafilm.

The samples were thermostated at 23.8°C in a constant temperature water bath. The exchange process was followed by removing the tubes from the bath at appropriate times, taking their ^1H NMR spectra, and returning the tubes to the bath. Peaks of the desired protons in the BT ligand were integrated against the Cp, Me, or H4 peaks, none of which underwent significant exchange under these conditions. This was verified by addition of 0.1 μl of an internal integration standard, t-BuOH, to the 0.20 *M* [KOH] runs with **1** and **2**. The data were collected until 55–70% exchange of the proton of interest had occurred. The timescale of these experiments ranged from 1 h (1.1 *M* [KOH]; **1**, H2) to 43 h (0.20 *M* [KOH]; **2**, H7).

The 0.0 *M* [KOH] run for **1** was performed by adding **1** (0.0046 g, 1.0×10^{-5} mol, 0.033 *M*) to an NMR tube containing 0.30 ml of CD_3OD. Without any KOH present, the polarity of the solution was too low to completely dissolve the compound. Integrals of H2 and H7 were monitored over a period of 143 h at 23.8°C. No exchange occurred. A similar experiment with **2** (0.0047 g, 1.0×10^{-5} mol, 0.033 *M*) showed that no exchange occurred over 90 h.

In order to determine whether uncoordinated BT undergoes base-catalyzed exchange under the conditions of these studies, the following experiment was performed. To 0.30 ml of a 1.1 *M* KOH/CD_3OD solution was added BT (approximately 0.005 g, 4×10^{-5} mol, 0.1 *M*), and the mixture was thermostated at 23.8°C. The integrals of H2 and H7 were monitored for 88 h during which time no exchange occurred. The exchange reaction for [CpRu(η-C_6H_6)]PF_6 was also performed. To 0.30 ml of a 1.1 *M* KOH/CD_3OD solution was added [CpRu(η-C_6H_6)]PF_6 (0.0051 g, 1.3×10^{-5} mol, 0.044 *M*). The NMR tube was thermostated at 23.8°C, and the integral of the benzene peak was monitored over a period of 116 h. No exchange occurred.

The observed rate constants, k_{obs}, were obtained from least-squares analyses of plots of ln I_{HX} versus time (I_{HX} is the integral of proton X, $X = 2$ or 7; $k_{obs} = -\text{slope}$) and are presented in Table 1. The correlation coefficients for these plots averaged 0.98; the error in the values is primarily a result of the ±5% error in the integration of the H2 and H7 resonances in ^1H NMR spectra of the exchange reactions. The second-order rate constants, k_{HX} ($X = 2$ or 7), in Fig. 2, were obtained from least-squares analyses of plots of $k_{obs,HX}$ versus [KOH]. The errors in the calculated values of k_{HX} are a result of errors in $k_{obs,HX}$ and in [KOH]

TABLE 1

Rate Constants, k_{obs}, for the KOH-Catalyzed Exchange of H2 and H7 in CD_3OD Solvent at 23.8°C

[KOH] (M)	$10^5k_{obs,H2}$ (s^{-1})	$10^5k_{obs,H7}$ (s^{-1})
	$[CpRu(BT)]PF_6$, **1**	
0.00	0.00	0.00
0.10	6.2	[a]
0.20	6.8	0.61
0.50	11	1.3
0.70	16	1.7
1.1	20	2.2
1.5	[b]	3.3
	$[CpRu(3\text{-}MeBT)]PF_6$, **2**	
0.00	0.00	0.00
0.20	1.2	0.58
0.50	1.6	0.76
0.70	2.4	1.3
0.90	2.8	1.3
1.1	3.7	1.4
1.3	4.3	1.8
1.5	5.0	2.2

[a] Too slow for accurate measurement.
[b] Too fast for accurate measurement.

due to small amounts of CH_3OH not being removed *in vacuo* from the standard KOH/ CH_3OH solution.

Catalyst Synthesis

The lead Chevrel phase catalyst, $PbMo_{6.2}S_8$, was prepared from stoichiometric amounts of 200 mesh, powdered molybdenum metal (reduced at 1000°C in hydrogen for 18 h), lead sulfide, and powdered sulfur. The mixture was ground together thoroughly, pressed into 13-mm pellets, and sealed in evacuated fused-silica tubes, which had been previously back-filled with argon to 20 in. Hg vacuum pressure. The tubes were heated slowly from 450 to 750°C for a period of 48–72 h in a muffle furnace, then immediately transferred to a high-temperature box furnace at 1200°C for 24 h, and quenched in air.

The unsupported $Co_{0.25}MoS$ catalyst (*18*) was synthesized by preparing material with a molar cobalt-to-molybdenum ratio of 1 : 4, using the homogeneous precipitation technique (*16*), followed by pretreatment at 450°C in 2% H_2S/H_2 for 4 h.

The supported rhenium catalyst was prepared by aqueous impregnation of Re_2O_7 into a calcined γ-Al_2O_3 support (Armak 03-331, 175 m^2/g) to give a 5% loading of Re by weight. The detailed procedure has been previously described (*17*). The catalyst was sulfided *in situ* by flowing 2 mol% BT/H_2 at the reaction temperature for approximately 5 h.

Catalyst Characterization

The purities of the $PbMo_{6.2}S_8$ and the $Co_{0.25}MoS$ catalysts were established by X-ray powder diffraction and laser Raman spectroscopy. A detailed description of the characterization methods and results has been previously given (*18*). The catalysts were stable under the reaction conditions; no changes in purity or formation of other phases were noted.

The supported Re catalyst was characterized before and after pretreatment by laser Raman spectroscopy, X-ray photoelectron spectroscopy, infrared spectroscopy, and thermogravimetric analysis (*17*). Raman spectra showed that none of the Re_2O_7

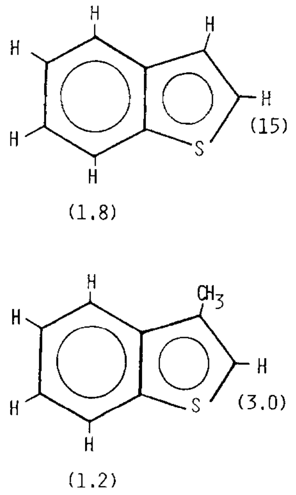


FIG. 2. Second-order rate constants, 10^5k_{HX} (M^{-1} s^{-1}), for deuterium exchange in the benzothiophene ligands of $[CpRu(BT)]^+$, **1**, and $[CpRu(3\text{-}MeBT)]^+$, **2**.

starting material was present in the catalyst. Slow heating rates were required (2°C/min) during reduction of the catalyst to prevent the loss of Re. This catalyst was also shown to be very resistant to sulfiding treatments and remained stable under reaction conditions.

Apparatus and Procedures

The reactor for these studies consisted of a $\frac{1}{4}$-in. stainless-steel tube in which the catalyst was held in place with a stainless-steel screen. Catalyst loadings were $PbMo_{6.2}S_8$ (0.336 g), $Co_{0.25}MoS$ (0.164 g), and 5% Re/γ-Al_2O_3 (0.199 g). Liquid BT (Aldrich, 97%) was fed to the system by a Sage 341 syringe pump from a 1-ml Hamilton "gas-tight" syringe. BT is a solid at room temperature (m.p. 29–32°C), therefore, it was necessary to heat a small chamber surrounding the syringe to 40°C. The BT was pumped into a saturator, which was maintained at 230°C and packed with glass beads, where it was mixed with hydrogen or deuterium and vaporized. All lines downstream of the saturator were wrapped in heating tape and maintained at 235°C. Product analysis was performed using a 3% SP-2100 on a 100–120 mesh Supelcoport column in an Antek 310 gas chromatograph with a Hewlett–Packard 3390A digital integrator. High-purity helium (99.997%) was used as the carrier gas at 19 ml/min (STP).

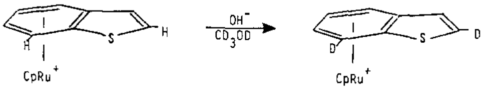
The reactor was heated from room temperature to the reaction temperature in a flow of helium (1–2 h) for the $Co_{0.25}MoS$ and $PbMo_{6.2}S_8$ catalysts and in a flow of high-purity H_2 (99.997%) (12 h) for the supported Re catalyst. The He or H_2 was then replaced by a continuous flow of 2 mol% BT in research-grade D_2 (99.99%) at 20 ml/min (STP). Reaction temperatures ranging from 250 to 500°C were used as shown in Table 3. The system was allowed to stabilize at the reaction temperature (0.5–1 h), as evidenced by constant conversion of BT to other compounds (% conversion = 100-[percentage of d_0–d_6 BT in product stream]), before the BT collection began. Experiments were also performed using either the empty reactor or γ-Al_2O_3 (0.143 g) in the reactor. These experiments were undertaken to observe the ability, if any, of the alumina support in the Re catalyst or of the stainless-steel reactor to catalyze deuterium exchange in benzothiophene.

The exchanged BT was collected from the reactor stream in a 7-mm Pyrex tube (cooled to 0°C) and was analyzed by mass spectrometry and ^1H and ^2H NMR. The error in integration of the ^1H NMR H2–H7 resonances (Table 3) is approximately ±10%.

RESULTS AND DISCUSSION

*Base-Catalyzed Deuterium Exchange of BT and 3-MeBT Protons in [CpRu(BT)]PF_6, **1**, and [CpRu(3-MeBT)]PF_6, **2***

The 2 and 7 protons of the BT and 3-MeBT ligands in complexes **1** and **2**, respectively, undergo base-catalyzed exchange with deuterium as shown in



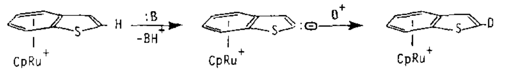
(4)

The kinetic data for this exchange reaction conform to the rate law,

$$-\frac{d[\mathrm{RuH}X]}{dt} = k_{\mathrm{H}X}[\mathrm{OH}^-][\mathrm{RuH}X] = k_{\mathrm{obs,H}X}[\mathrm{RuH}X],$$

where [RuHX] is the concentration of the unexchanged ruthenium complex **1** or **2**. The values calculated for k_{obs} are given in Table 1. From plots of $k_{\mathrm{obs,H}X}$ versus $[OH^-]$ the second-order rate constants, $k_{\mathrm{H}X}$, are obtained. The results are presented in Fig. 2. Only H2 and H7 are observed to exchange under the conditions of the studies.

The first-order dependence of the exchange on $[OH^-]$ suggests that the slow step of the mechanism is proton abstraction from the Ru complex as has been proposed previously for deuterium exchange in T of $[CpRuT]^+$ (*8*). The mechanism for H2 exchange reaction may be depicted as in



(5)

The H2 exchanges much more readily than H7 in **1** ($k_{H2} = 15 \times 10^{-5}\ M^{-1}\ s^{-1}$, $k_{H7} = 1.8 \times 10^{-5}\ M^{-1}\ s^{-1}$), but k_{H2} decreases significantly upon substitution of a methyl group in the 3 position (for **2**, $k_{H2} = 3.0 \times 10^{-5}\ M^{-1}\ s^{-1}$, $k_{H7} = 1.2 \times 10^{-5}\ M^{-1}\ s^{-1}$). This decrease would be expected on the basis of the proposed mechanism since an electron-donating 3-Me group would decrease the acidity of the H2 proton. A similar decrease is observed in the thiophene complexes, where the second-order rate constant for H4 exchange in $[CpRu(T)]^+$ is approximately seven times greater than k_{H4} for $[CpRu(3\text{-}MeT)]^+$ (*8a*). The H7 rate constant for **1** and **2** is not greatly affected by methyl substitution.

An alternative mechanism, which would proceed via initial attack of OH^- at C3, followed by D^+ addition at C2 and then stepwise loss of H^+ from C2 and OH^- from C3, cannot be ruled out on the basis of the kinetic data assuming that the addition of OH^- is the rate-determining step and that all subsequent steps are rapid. However, nucleophilic addition (H^-) to **1** and to the related complex, $[(\eta\text{-}C_5(CH_3)_5)Ir(\eta^6\text{-}BT)](BF_4)_2$($H^-$, OCH_3^-, $SCH_2CH_3^-$, $CH(CO_2CH_3)_2^-$, and $P(CH_3)_3$), is known to occur preferentially at the 7 position (*14*), and there were no peaks in the ^1H NMR spectra of the exchange reactions which would suggest that OH^- adduct formation had occurred. Therefore, the alternative mechanism seems less reasonable than that presented in Eq. (5).

The protons (H2 and H7) exchanged in **1** and **2** are at positions different from those exchanged in the base-catalyzed exchange reaction of uncoordinated BT, which has been reported to occur in the 2 and 3 positions (*19*). Zatsepina and co-workers (*19b*) determined rate constants for deuterium exchange in BT in 0.57 *N* EtOK/EtOD between 50 and 150°C. The H2 (k_{obs}, 80°C = $9.1 \times 10^{-5}\ s^{-1}$) exchanged faster than H3 (k_{obs}, 120°C = $0.23 \times 10^{-5}\ s^{-1}$) but much slower than H2 in either **1** or **2**. Therefore, H7 and H2 of **1** and **2** are strongly activated to exchange by coordination of BT to Ru. However, H2 is not as strongly activated in **1** and **2** as it is in $[CpRu(T)]^+$ ($k_{H2} > 1.5\ M^{-1}\ s^{-1}$) where the T ring is directly coordinated to the transition metal center. The observed rate constant for H2 exchange in uncoordinated T ($3.3 \times 10^{-5}\ s^{-1}$ at 80°C) is less than that in BT (*19b*). It is possible that H3 in **1** is also activated but still does not exchange at a measurable rate under these conditions. The presence of the sulfur atom and the coordination of the benzene ring of BT to $CpRu^+$ both clearly play an important role in activating H7 and H2 to exchange. No exchange of the benzene ring protons in $[CpRu(\eta\text{-}C_6H_6)]^+$ was observed after 116 h in 1.1 *M* KOH at 23.8°C.

Deuterium Exchange of BT Protons over HDS Catalysts

The results of the heterogeneous reactor studies are given in Table 2. The percentage deuteration (±5%) of the BT for each of the runs in Table 2 was calculated from the mass spectrum of the product; corrections for the $M + 1$ and $M + 2$ peaks, due to the ^{13}C and ^{34}S isotopes, were made. For all the catalysts studied, the average number of deuterium atoms exchanged into BT, d_{ave}, generally increased with increasing temperature and percentage conversion for a given catalyst. The d_{ave} values also increased with temperature on $\gamma\text{-}Al_2O_3$, No significant exchange was observed for BT run through the empty reactor at 400°C. The 5% $Re/\gamma\text{-}Al_2O_3$ catalyst appears to be the most effective at catalyzing deuterium exchange. At 13% conversion (400°C) the $d_{ave} = 4.4$.

The random exchange values were calculated from the binomial expansion of $(H + D)^6$ where H and D represent the fraction of

TABLE 2

Results of Deuterium Exchange of BT over Heterogeneous HDS Catalysts

Catalyst	Reactor temperature (°C)	Conversion (%)	% deuteration[a]							d_{ave}
			d_0	d_1	d_2	d_3	d_4	d_5	d_6	
$PbMo_{6.2}S_8$	450	2	21(23)	42(38)	27(27)	7(10)	2(2)	1(0)	0(0)	1.3
$PbMo_{6.2}S_8$	500	6	14(18)	40(36)	34(30)	9(13)	2(3)	1(0)	0(0)	1.5
$Co_{0.25}MoS$	250	8	3(3)	17(15)	41(29)	15(30)	9(17)	8(5)	7(1)	2.6
$Co_{0.25}MoS$	300	27	2(3)	13(14)	37(28)	25(30)	12(18)	8(6)	3(1)	2.7
$Co_{0.25}MoS$	350	86	3(3)	12(13)	36(28)	24(30)	13(19)	8(6)	4(1)	2.7
5% Re/γ-Al_2O_3	300	1	4(8)	13(24)	61(32)	17(24)	3(10)	1(2)	1(0)	2.1
5% Re/γ-Al_2O_3	350	6	1(1)	4(8)	31(22)	30(31)	21(25)	10(11)	3(2)	3.1
5% Re/γ-Al_2O_3	400	13	2(0)	2(1)	11(4)	11(14)	16(31)	26(34)	32(16)	4.4
γ-Al_2O_3	250	0	43(37)	34(40)	16(18)	4(4)	2(1)	1(0)	0(0)	0.9
γ-Al_2O_3	300	0	16(16)	32(33)	36(31)	10(15)	4(4)	2(1)	0(0)	1.6
γ-Al_2O_3	350	0	5(3)	8(14)	30(28)	30(30)	18(19)	7(5)	2(1)	2.7
None	400	0	97(97)	3(3)	0(0)	0(0)	0(0)	0(0)	0(0)	0.03

[a] The values in parentheses represent the random exchange value calculated from the binomial expansion of $(H + D)^6$ where $D = d_{ave}/6$ and $H = (1 - D)$.

hydrogen, and deuterium, exchanged in each molecule of BT. Although the γ-Al_2O_3 runs resulted in significant exchange of BT (d_{ave} = 0.91 (250°C), 1.6 (300°C), 2.7 (350°C)) the distribution of the d_0–d_6 BT species is clearly random. Nevertheless, the ^1H NMR spectra of the BT from the γ-Al_2O_3 experiments show (Table 3) that the 2 and 3 positions are preferentially exchanged (the integrals for H4–H7 were all of approximately the same magnitude). Essentially random distribution of the d_0–d_6 BT species is also found for $PbMo_{6.2}S_8$. However, in the $Co_{0.25}MoS$ and 5% Re/γ-Al_2O_3 runs the d_0–d_6 distribution is nonrandom and in most cases the greatest deviation occurs in the high percentages of BT-d_2 found in the exchanged BT. This indicates that two of the BT positions are activated toward exchange by the catalyst. Integrals of the resonances in the ^1H NMR spectra (acetone-d_6, Table 3) of the exchanged BT clearly show that these are the 2 and 3 positions for all runs.

TABLE 3

Integrals from ^1H NMR Spectra of Exchanged BT[a]

Catalyst	Temperature (°C)	H2	H3	H4	H5	H6	H7
$PbMo_{6.2}S$	400	58	102	101	187		100
$PbMo_{6.2}S$	450	62	106	100	189		100
$PbMo_{6.2}S$	500	38	91	102	183		100
$Co_{0.25}MoS$	250	5	28	101	165		100
$Co_{0.25}MoS$	300	10	20	87	198		100
$Co_{0.25}MoS$	350	5	34	112	199		100
5% Re/γ-Al_2O_3	300	10	30	99	183		100
5% Re/γ-Al_2O_3	350	5	14	99	193		100
5% Re/γ-Al_2O_3	400	1	24	102	250		100
γ-Al_2O_3	250	52	82	106	202		100
γ-Al_2O_3	300	31	31	93	184		100
γ-Al_2O_3	350	16	38	93	212		100
None	400	85	107	106	199		100

[a] Integrals are relative to that of the H7 resonance which was set to 100.

Cowley also reported deuterium exchange of H2 and H3 of BT for experiments performed with D_2 gas over a sulfided Co–Mo/Al_2O_3 catalyst (*6c*). He interpreted his results as suggesting that BT was π-bound through the thiophene ring of BT on the surface of the catalyst as opposed to S-bound since he proposed that S-bound BT would give rise to H2 and H7 exchange because of their close proximity to the catalyst surface in the S-bound form. The exchange of BT over the catalyst was proposed by Cowley to occur via σ-complex formation as shown in Fig. 3 for H2 exchange; a similar series of reactions would describe exchange of H3 (*6c*). The first step of this sequence can be considered analogous to electrophilic attack at C2 by Mo^{3+}. It is known that BT undergoes electrophilic attack preferentially at C3 rather than C2; this is supported both experimen-

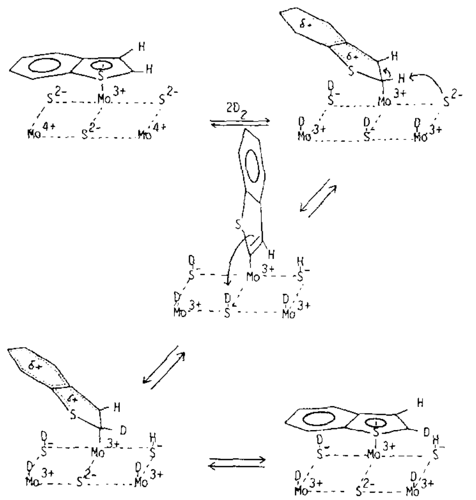
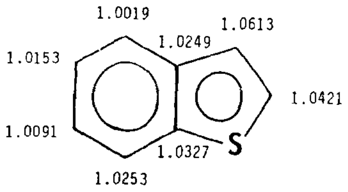


FIG. 3. Cowley's proposed mechanism for deuterium exchange, shown for H2 (*6c*).

tally (*20*) and by MO calculations (*21*) which give the π-electron densities at C2–C9 (Insert 1). The higher electron density at C3 suggests that H3 might exchange faster than H2. However, we find that H2 is more readily exchanged than H3 over HDS catalysts (Table 3). Alternatively, the exchange could occur by deprotonation of a π-thiophene-coordinated BT, by a basic site such as S^{2-}, without σ-complex formation. The base-catalyzed exchange reactions of T and BT in $CpRu^+$ complexes provide precedent for direct deprotonation of π-bound thiophenic compounds.



In all of the samples (Table 2), significant percentages of BT-d_3 were also produced in addition to BT-d_2. It was of interest to determine if the third deuterium was preferentially exchanged into any of the positions on the benzene ring of BT, particularly in view of the relatively rapid exchange of H7 in $[CpRu(BT)]^+$. However, the resonances of H4–H7 in the deuterated BT integrated to approximately the same values for all of the runs (Table 3). Therefore, the ^2H NMR spectrum of the deuterated BT from the $Co_{0.25}MoS$ (300°C) experiment was obtained. The integrals of the deuterium resonances were D2(208), D3(202), D4(60), D5 and D6(100), and D7(40), which clearly illustrate the high degree of 2 and 3 exchange which had occurred as well as the lack of marked preference for exchange at any one of the 4, 5, 6, or 7 positions.

CONCLUSIONS

In earlier studies (*8, 22*), we observed that patterns of deuterium exchange of thiophene and methyl-substituted thiophenes with D_2 over HDS catalysts were very similar to those observed for base-catalyzed deuterium exchange in the same thiophenes in the complexes $CpRu(thiophene)^+$ (Eq. (2)). While these comparisons did not prove that these exchanges occur by similar mechanisms, we proposed that π-adsorbed thiophenes on HDS catalysts may be activated to exchange in a manner similar to that in $CpRu(thiophene)^+$. Thus, π-adsorbed thiophenes could be deprotonated by a basic site, such as an oxide or sulfide, on the catalyst and then deuterated by a surface OD or SD group.

In contrast to the thiophene situation, the analogous studies of BT and 3-MeBT described in this paper show that the patterns of deuterium exchange are quite different in $CpRu(BT)^+$ and over HDS catalysts. In $CpRu(BT)^+$, H2 and H7 undergo deuterium exchange, while over several HDS catalysts, BT undergoes exchange in the 2 and 3 positions and there is no activation of a particular position on the benzene ring. Thus, $CpRu(BT)^+$ is not a viable model for BT exchange on HDS catalysts. A reason for it being a poor model is that in $CpRu(BT)^+$ and $CpRu(3\text{-}MeBT)^+$ it is the benzene ring of the benzothiophene that is coordinated to the Ru and therefore activated. In order to account for preferential exchange in the thiophene ring (H2 and H3) over HDS catalysts, a model involving π-coordination of the thiophene ring would probably be more successful. However, in all known complexes (*14, 23*), including those involving Ru, Rh, Ir, and Cr, the BT is π-coordinated via the benzene ring. This suggests that BT might also prefer to π-bond to HDS catalysts via the benzene ring. If it does so, it is unlikely to promote the observed exchange at H2 and H3. Therefore, we propose that while BT may prefer to adsorb to a metal site via the π-benzene ring, it undergoes very slow exchange in this form, as in $CpRu(BT)^+$. To account for the preferred H2 and H3 exchange, we suggest that a small equilibrium amount of BT is adsorbed via the π-thiophene ring and in this form is activated to undergo deuterium exchange at the H2 and H3 positions as in CpRu $(thiophene)^+$. The mechanism of this exchange would presumably be similar to that suggested above for thiophene.

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REFERENCES

1. Gates, B. C., Katzer, J. R., and Schuit, G. C. A., "Chemistry of Catalytic Processes," p. 392. McGraw–Hill, New York, 1979.
2. (*a*) Schuman, S. C., and Shalit, H., *in* "Catalysis Reviews" (H. Heinemann, Ed.), p. 246. Dekker, New York, 1971; (*b*) Satterfield, C. N., "Heterogeneous Catalysis in Practice," p. 260. McGraw–Hill, New York, 1980.
3. (*a*) Schuit, G. C. A., and Gates, B. C., *AIChE J.* **19,** 417 (1973); (*b*) Kwart, H., Schuit, G. C. A., and Gates, B. C., *J. Catal.* **61,** 128 (1980); (*c*) Lopez, R., Peter, R., and Zdrazil, M., *J. Catal.* **73,** 406 (1982); (*d*) Van Parijs, I. A., Hosten, L. H., and Froment, G. F., *Ind. Eng. Prod. Res. Dev.* **25,** 437 (1986).
4. Kemball, C., *Chem. Soc. Rev.* **13,** 375 (1984).
5. McCarty, K. F., and Schrader, G. L., *J. Catal.* **103,** 261 (1987).
6. (*a*) Blake, M. R., Eyre, M., Moyes, R. B., and Wells, P. B., *Stud. Surf. Sci. Catal.* **7,** 591 (1981); (*b*) Behbahany, F., Sheikhrezai, Z., Djalali, M., and Salajegheh, S., *J. Catal.* **63,** 285 (1980); (*c*) Cowley, S. W., Ph.D. thesis, Southern Illinois University, Carbondale, 1975; (*d*) Mikovsky, R. J., Silvestri, A. J., and Heinemann, H., *J. Catal.* **34,** 324 (1974); (*e*) Smith, G. V., Hinckley, C. C., and Behbahany, F., *J. Catal.* **30,** 218 (1973); (*f*) Kieren, P., and Kemball, C., *J. Catal.* **4,** 394 (1965).
7. (*a*) Geneste, P., Amblard, P., Bonnet, M., and Graffin, P., *J. Catal.* **61,** 115 (1980); (*b*) Rollman, L. D., *J. Catal.* **64,** 243 (1977).
8. (*a*) Sauer, N. N., and Angelici, R. J., *Organometallics* **6,** 1146 (1987); (*b*) Spies, G. H., and Angelici, R. J., *J. Amer. Chem. Soc.* **107,** 5569 (1985).
9. Kilanowski, D. R., and Gates, B. C., *J. Catal.* **62,** 70 (1980).
10. Singhal, G. H., Espino, R. L., and Sobel, J. E., *J. Catal.* **35,** 353 (1974).
11. (*a*) Bartsch, R., and Tanielian, C., *J. Catal.* **35,** 353 (1974); (*b*) Givens, E. N., and Venuto, P. B., *Prepr. Amer. Chem. Soc. Div. Pet. Chem.* **15,** A 183 (1970).
12. (*a*) Pokorny, P., and Zdrazil, M., *Collect. Czech. Chem. Commun.* **46,** 2185 (1981); (*b*) Kilanowski, D. R., Teeuwen, H., deBeer, V. H. J., Gates, B. C., Schuit, G. C. A., and Kwart, H., *J. Catal.* **55,** 129 (1978); (*c*) Furimsky, E., and Amberg, C. H., *Canad. J. Chem.* **54,** 1507 (1976).
13. (*a*) Nag, N. K., Sapre, A. V., Broderick, D. H., and Gates, B. C., *J. Catal.* **57,** 509 (1979); (*b*) Zdrazil, M., *Collect. Czech. Chem. Commun.* **42,** 1484, (1977); (*c*) Mitchell, P. C. H., *Catalysis* **4,** 175 (1981).
14. (*a*) Huckett, S. C., Miller, L.L., Jacobson, R. A., and Angelici, R. J., *Organometallics* **7,** 686 (1988); (*b*) Huckett, S. C., and Angelici, R. J., *Organometallics,* in press.
15. Gill, T. P., and Mann, K. R., *Organometallics* **1,** 485 (1982).
16. Candia, R., Clausen, B. S., and Topsoe, H., *Bull. Chim. Belg.* **90,** 1225 (1981).
17. Markel, E. J., M.S. Thesis, Iowa State University, Ames, 1986.
18. McCarty, K. F., and Schrader, G. L., *Ind. Eng. Chem. Prod. Res. Div.* **23,** 519 (1984).
19. (*a*) Yakushina, T. A., Shapiro, I. O., Zvyagintseva, E. V., Litvinov, V. P., Ozolins, S., Gol'dfarb, Y. L., and Shatenshtein, A. I., *Zh. Obshch. Khim.* **41,** 1930 (1971); *Chem. Abstr.* **76,** 24481 (1972); (*b*) Zatsepina, N. N., Kaminskii, Y. L., and Tupitsyn, I. F., *Reakts. Sposobn. Org. Soedin.* **6,** 753 (1969).
20. Scrowston, R. M., *Adv. Heterocylc. Chem.* **29,** 171 (1981).
21. Klasnic, L., Pop, E., Trinajstic, N., and Knop, J. V., *Tetrahedron* **28,** 3465 (1972).
22. Hachgenei, J. W., and Angelici, R. J., *Organometallics,* submitted for publication.
23. (*a*) King, R. B., and Stone, F. G. A., *J. Amer. Chem. Soc.* **82,** 4557 (1960); (*b*) Fischer, E. O., Goodwin, H. A., Kreiter, C. G., Simmons, H. D., Jr., Sonogashira, K., and Wild, S. B., *J. Organomet. Chem.* **14,** 359 (1968).