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(η-Thiophene)Ru(η-C_5H_5)$^+$ as a Model for the Adsorption and Deuterium Exchange of Thiophenes on Hydrodesulfurization Catalysts

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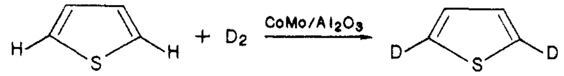
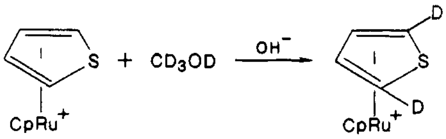
As a model for the observed exchange of thiophene protons with D_2 over hydrodesulfurization (HDS) catalysts, rates of exchange of thiophene protons in CpRu(η-thiophene)$^+$ complexes, where thiophene is thiophene, 2- or 3-methylthiophene (2- or 3-MT), or 2,5-dimethylthiophene (2,5-DMT), were studied in CD_3OD solvent in the presence of OH^-. The exchanges follow a rate law, rate = k[CpRu(thiophene)$^+$][OH^-], which suggests a mechanism involving rate-determining proton abstraction from the thiophene by OH^-, followed by deuteriation (D^+) by the solvent. The fastest exchange occurs at the carbons adjacent (α) to the sulfur; slower exchange occurs at the β-positions; the slowest exchange occurs at the methyl substituents. This same order of reactivity is observed in exchange reactions of methyl-substituted thiophenes over HDS catalysts. These results suggest that deuterium exchange on HDS catalysts occurs via thiophene π-bonded to a metal site (e.g., Mo). This coordination activates the thiophene to deprotonation by a basic site (e.g. S^{2-} or O^{2-}), which is followed by deuteriation by SD^- or OD^- groups present on the catalyst surface.

Catalytic removal of sulfur from organosulfur compounds in petroleum is accomplished industrially over a cobalt-promoted molybdenum catalyst at high temperatures and elevated H_2 pressures in a process known as hydrodesulfurization (HDS).[2,3] Despite a tremendous number of studies attempting to elucidate specific steps in this process, many key questions about the mechanism remain.[4] Thiophene, one of the sulfur-containing compounds that is most difficult to desulfurize, undergoes, prior to desulfurization, extensive exchange (eq 1) with



(1)

deuterium on the catalyst if D_2 is used in the reaction. Exchange occurs primarily at the 2- and 5- (α) positions of the ring with much smaller amounts being incorporated at the 3- and 4-(β) positions.[5] This exchange pattern has frequently been used as evidence to support the proposal that thiophene binds to HDS catalysts through an "end on" attachment, i.e., through its sulfur atom only.[5a,c] Presumably, such an adsorption mode would selectively activate the 2- and 5-hydrogens toward deuterium exchange by placing them in close proximity to the catalyst surface. However, recent studies designed to probe the surface attachment of thiophene to the catalyst surface suggest that a π-bound adsorption mode is more likely.[5d,6,7] Indeed, model studies have shown[8] that π-thiophene ligands in transition-metal complexes are highly activated to undergo reactions analogous to those suggested to occur on the catalyst. Among these reactions is the rapid exchange[8c] of the hydrogens at the 2- and 5-positions of thiophene in [CpRu(thiophene)]BF_4, Cp = η-C_5H_5, in the presence of bases in methanol-d_4 (eq 2); no exchange is



(2)

observed at the 3- and 4-positions over short periods of time (<15 min). This complex was also found to exchange over Al_2O_3 which was deuteriated with D_2O.[8c]

As for thiophene over HDS catalysts, methylthiophenes undergo more rapid exchange in the 2- and 5-positions than in the 3- and 4-positions; the least amount of exchange occurs in the CH_3 groups.[5a] For the purpose of comparing relative rates of deuterium exchange over heterogeneous catalysts with those of model complexes with π-bound thiophene ligands, we report herein kinetic studies of base-promoted deuterium exchange in [CpRu(thiophene)$^+$], where thiophene represents thiophene, 2-methylthiophene, 3-methylthiophene, and 2,5-dimethylthiophene. The relative rates of exchange that we observe strongly support π-bound thiophenes as intermediates in their exchange with deuterium over HDS catalysts.

Experimental Section

General Procedures. Kinetic studies were performed on a Bruker WM-300 NMR spectrometer. All other ^1H NMR and ^{13}C NMR spectra were recorded on a Nicolet NT-300 spectrometer. Chemical shifts are referenced to internal $(CH_3)_4Si$ by using deuteriated solvents as internal locks. FAB mass spectra were obtained on a Kratos MS-50 mass spectrometer. Elemental analyses were performed by Galbraith Laboratories Inc. The thiophene complex [CpRu(thiophene)]PF_6 (1) was prepared as previously described.[8b,c] The 2- and 3-methylthiophenes (2-MT and 3-MT) and 2,5-dimethylthiophene (2,5-DMT) (Aldrich) were distilled over CaH_2 at ambient pressure before use. Methylene

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chloride and CH_3CN were distilled from CaH_2 and stored over 4-Å molecular sieves prior to use. Diethyl ether, acetone, and 1,2-dichloroethane were used without further purification. The standardized 0.50 M KOH in methanol solution was purchased from Aldrich and used without further purification. The 99.5% D CD_3OD was purchased from Norell Inc. and stored over 4-Å molecular sieves prior to use. Methanol was distilled from CaH_2 under N_2.

Preparations of [CpRu(η-2-MT)]BF_4 (2) and [CpRu(η-2,5-DMT)]BF_4 (4). Method I. The complex $CpRu(PPh_3)_2Cl$[9] (1.00 g, 1.38 mmol), $AgBF_4$ (0.290 g, 1.52 mmol), and 3 mL of 2-MT or 2,5-DMT were refluxed in 20 mL of CH_3OH for 24 h under N_2. Isolation of the product was accomplished by removing the volatiles from the reaction mixture in vacuo, extracting the residue with CH_2Cl_2, and precipitating the product from the filtered solution by slow addition of Et_2O. Successive recrystallizations from CH_2Cl_2/Et_2O yielded the salts as brown powders (yield ca. 40% for both complexes). [CpRu(η-2-MT)]BF_4: ^1H NMR ($CDCl_3$) δ 5.39 (s, C_5H_5), 6.29 (m, H_3 and H_4), 6.13 (d, H_5), 2.42 (s, Me); ^{13}C NMR ($CDCl_3$) δ 80.93 (C_5H_5), 86.80, 86.18, 77.90 (C_{3-5}), 80.43 (C_2), 15.59 (Me); MS (FAB, glycerol), *m/e* 265 (M^+). Anal. Calcd for $C_{10}H_{11}BF_4RuS$: C, 34.21; H, 3.16; S, 9.13. Found: C, 34.32; H, 3.17; S, 8.93. [CpRu(η-2,5-DMT)]BF_4: ^1H NMR ($CDCl_3$) δ 5.35 (s, C_5H_5), 6.23 (s, $H_{3,4}$), 2.37 (s, Me); ^{13}C NMR ($CDCl_3$) δ 81.04 (C_5H_5), 86.89 ($C_{3,4}$), 82.38 ($C_{2,5}$), 15.77 (Me); MS (FAB, glycerol), *m/e* 279 (M^+). Anal. Calcd for $C_{11}H_{13}BF_4RuS$: C, 36.18; H, 3.59; S, 8.78. Found: C, 36.38; H, 3.64; S, 9.20.

Method II. As described by Mann et al.,[10] [CpRu(η-C_6H_6)]PF_6 (0.552 g, 1.42 mmol) was photolyzed in 280 mL of CH_3CN to give $[CpRu(NCCH_3)_3]PF_6$. The solvent was then removed in vacuo. The remaining oily solid was dissolved in 25 mL of $ClCH_2CH_2Cl$ containing 4 mL of 2-MT. After the solution was refluxed for 16 h under N_2, the volatiles were removed in vacuo, and the residue was extracted with a minimum of warm acetone. After the insoluble material was filtered off, the product was precipitated with Et_2O as a pale brown solid, yield 0.348 g, 60%. The ^1H NMR spectrum of [CpRu(η-2-MT)]PF_6 was identical with that of [CpRu(η-2-MT)]BF_4 (2) prepared by method I.

[CpRu(η-C_6H_6)]BF_4 (0.260 g, 0.785 mmol), prepared as described by Mann et al.[10] for the PF_6^- salt using $[NH_4]BF_4$ instead, was photolyzed in 280 mL of CH_3CN. The solution containing $[CpRu(NCCH_3)_3]BF_4$ was evaporated to dryness and refluxed in 25 mL of $ClCH_2CH_2Cl$ with 4 mL of 2,5-DMT for 16 h. The reaction mixture was worked up as described for [CpRu(η-2-MT)]BF_4, method II; yield 0.332 g, 60%. The ^1H NMR spectrum of the product was identical with that of [CpRu(η-2,5-DMT)]BF_4 (4) prepared by method I.

Preparation of [CpRu(η-3-MT)]BF_4 (3). With use of method II, [CpRu(η-C_6H_6)]BF_4 (0.250 g, 0.753 mmol) was photolyzed in 280 mL of CH_3CN for 24 h. The CH_3CN was removed in vacuo, and the brown residue $[CpRu(NCCH_3)_3]BF_4$ was dissolved in 30 mL of $ClCH_2CH_2Cl$; 4 mL of 3-MT was added, and the mixture was refluxed for 24 h. The $ClCH_2CH_2Cl$ was removed under vacuum, and the brown solid was recrystallized from hot acetone/diethyl ether: yield 0.122 g, 0.35 mmol, 46%; ^1H NMR (acetone-d_6) δ 5.48 (s, Cp), 6.58 (d, J = 2.96 Hz, H_5), 6.41 (s, H_2), 6.39 (d, J = 2.96 Hz, H_4), 2.46 (s, Me); ^{13}C NMR (acetone) δ 81.27 (C_5H_5), 88.46, 79.66, 79.24 ($C_{2,4,5}$), 69.14 (C_3), 14.75 (CH_3).

Kinetic Measurements. Rates of deuterium exchange into the thiophene complexes were measured by following the disappearance of the appropriate ^1H NMR peaks with time. Reactions of the thiophene complexes 1–4 with base were carried out under a N_2 atmosphere in NMR tubes sealed with rubber septa. The thiophene compound of interest was placed in the NMR tube under N_2, and methanol-d_4 was added by syringe. Samples were thermostated in the probe of the NMR spectrometer at 23 ± 1 °C for 10 min; then the 0.50 M KOH/CH_3OH solution was added by microliter syringe to give the desired KOH concentration. The NMR tube was lowered back into the probe of the NMR, the NMR shimmed, and the data acquisition started. For a typical sample, 4 min passed between the time the base was added and data collection was begun. For most samples, the disappearance of the thiophene protons was monitored by periodic integration against the Cp ring protons of the complex. For several samples, [CpRu(η-thiophene)]PF_6 (1) with 0.0150 M KOH and 0.0875 M KOH and [CpRu(η-2-MT)]PF_6 (2) with 0.050 M KOH, an internal standard of *tert*-butyl alcohol was added. The Cp ring and exchanging H_3 and H_4 proton signals were integrated relative to the *tert*-butyl alcohol. While the resonances for H_3 and H_4 decreased, no exchange of the Cp ring protons was observed. For the remaining samples, decrease of the H_3 and H_4 resonances was determined by integration against the Cp ring. Analysis of the exchange data was done by using the McKay equation, which is also the equation for a pseudo-first-order reaction;[11] linear plots of ln $(1 - F)$ vs. t (F = the fraction of exchange which had occurred) give a slope, k_{obsd}. Values of $(1 - F)$ were obtained from the integrated area of the proton of interest, $F = (A_0 - A_t)/A_0$, where A_0 is the integrated area before base addition and A_t is the area at time t. The rate constants, k_{obsd}, were obtained from least-squares analysis of plots of ln $(1 - F)$ vs. t which were linear for at least 75% of the reaction. In all reactions, concentrations of CD_3OD were at least 50 times that of the thiophene compound. For all compounds, 1–4, deuterium exchange of $H_{3,4}$ was observed to go to completion. Several of the free thiophenes were tested to see if they exchanged in the presence of base in CD_3OD. No exchange of 2- or 3-MT in 0.050 M KOH in CD_3OD was observed over a period of 60 h. Likewise, no exchange of thiophene was seen in 0.35 M KOH in CD_3OD over 24 h.

Exchange Preparation of [CpRu(η-thiophene-d_4)]PF_6. [CpRu(η-thiophene)]PF_6 (1) (0.030 g, 0.076 mmol) was dissolved in dry degassed CH_3OD (20 mL), and 0.50 M KOH in CH_3OH (0.75 ml) was added by syringe. The solution was stirred for 8 h, at which time exchange of all four thiophene protons was observed to be complete by ^1H NMR. Gaseous CO_2 was bubbled through the solution for 1 h to neutralize the base, and the solvent was removed. The residue was extracted with a minimum of freshly distilled CH_2Cl_2, and the product was precipitated by addition of Et_2O. The product was recrystallized from CH_2Cl_2/Et_2O two more times. The [CpRu(η-thiophene-d_4)]PF_6 was identified by its ^1H NMR and mass spectrum.

Based-Catalyzed Exchange of [CpRu(η-thiophene-d_4)]PF_6 with CH_3OH. [CpRu(η-thiophene)]PF_6 (0.025 g, 0.063 mmol) was dissolved in CH_3OH (9 mL). The mixture was immersed in a constant temperature bath (25.0 °C) and 0.50 M KOH in CH_3OH (1 mL) was added by syringe. One-milliliter samples were removed at different times to monitor the exchange; the base in each sample was neutralized by bubbling CO_2 through the solution for 30 min, and the CH_3OH solvent was removed in vacuo. The residue was dissolved in acetone-d_6, and the ^1H NMR spectrum was taken. The extent of exchange was determined by integrating the thiophene proton signals of the product 1. Positions 2 and 5 exchange completely within 10 min. The $H_{3,4}$ signals appeared much more slowly and were integrated relative to the $H_{2,5}$ peaks.

Results

Rate constants, k_{obsd}, for the KOH-catalyzed deuterium exchange reactions, e.g., eq 3, of 1–4 with CD_3OD are given

$$CpRu(SC_4H_4)^+ \xrightarrow[CD_3OD]{OH^-} CpRu(SC_4H_{4-x}D_x)^+ \quad (x = 1\text{–}4) \tag{3}$$

in Table I. As discussed below, detailed kinetic studies were possible only for the exchange of the $H_{3,4}$ protons. All reactions can be fit to the rate expression

$$-\frac{d[Ru]}{dt} = k[Ru][OH^-] = k_{obsd}[OH^-] \tag{4}$$

where [Ru] represents the concentration of complexes 1–4. Values for the second-order rate constants k (Table II) were obtained from slopes of plots of k_{obsd} vs. $[OH^-]$. In each of these plots, k_{obsd} had a small intercept value at

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Table I. k_{obsd} Rate Constants for KOH-Catalyzed Exchange of $H_{3,4}$ in Complexes 1–4 in CD_3OD at 23 °C

10^2[KOH], M	10^4k_{obsd}, s^{-1}	10^2[KOH], M	10^4k_{obsd}, s^{-1}
[CpRu(thiophene)]PF_6 (**1**) (1.39 × 10^{-2} M)			
0.875	0.78	3.75	2.7
1.25	1.1	5.00	3.7
2.50	2.0		
[CpRu(2-methylthiophene)]BF_4 (**2**) (3.13 × 10^{-2} M)			
1.50	0.43	7.50	1.5
2.50	0.68	8.75	1.8
5.00	1.1		
[CpRu(3-methylthiophene)]BF_4 (**3**) (3.65 × 10^{-2} M)			
2.50	0.35	10.0	1.2
5.00	0.60	12.5	1.5
8.75	1.0		
[CpRu(2,5-dimethylthiophene)]BF_4 (**4**) (3.02 × 10^{-2} M)			
8.75	0.32	16.0	0.69
10.0	0.42	20.0	0.71
12.5	0.61		

Table II. Second-Order Rate Constants, *k*, for Exchange of $H_{2,5}$, $H_{3,4}$, and CH_3 in Complexes 1–4 at 23 °C in CD_3OD Solvent

	10^3k, M^{-1} s^{-1}
$H_{2,5}$	
[CpRu(thiophene)]PF_6 (**1**)	>1500
[CpRu(2-methylthiophene)]BF_4 (**2**)	>1500
[CpRu(3-methylthiophene)]BF_4 (**3**)	>1500
$H_{3,4}$	
[CpRu(thiophene)]PF_6 (**1**)	8.0
[CpRu(2-methylthiophene)]BF_4 (**2**)	2.4
[CpRu(3-methylthiophene)]BF_4 (**3**)	1.2
[CpRu(2,5-dimethylthiophene)]BF_4 (**4**)	0.35
CH_3	
[CpRu(2-methylthiophene)]BF_4 (**2**)	0.20[a]
[CpRu(2,5-dimethylthiophene)]BF_4 (**4**)	0.005[a]

[a] Estimated, see text.

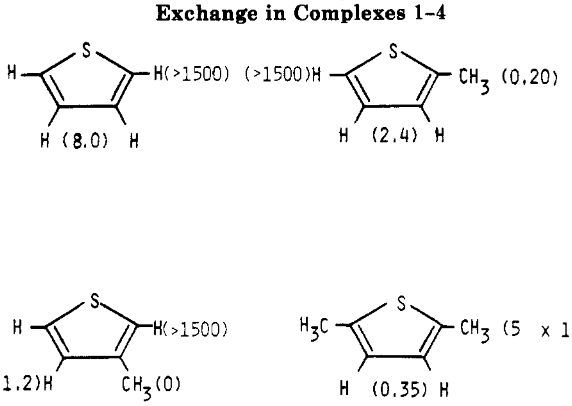
$[OH^-]$ = 0.00 M. These small intercepts are probably within experimental error of zero. In fact, there was no measurable deuterium exchange of $H_{3,4}$ when [CpRu(η-thiophene)]BF_4 reacted with CD_3OD in the absence of KOH for 20 h; in the presence of the base concentrations used in the kinetic studies (Table I), the exchange of these protons was complete within 6 h.

In all complexes (**1**–**3**), deuterium exchange of the H_2 and H_5 protons was too fast to follow by our ^1H NMR method. Complexes **1**–**3** in the presence of 1.00 × 10^{-3} M KOH (>60:1 ratio of complex:KOH) gave complete exchange of $H_{2,5}$ in less than 3 min. A lower limit on the rate constant, *k*, for this exchange was estimated (for $t_{1/2}$ = 90 s, $[OH^-]$ = 1.00 × 10^{-3} M) to be 1.5 M^{-1} s^{-1}. In a separate experiment, H_2 and H_5 in [CpRu(η-thiophene)]BF_4 were found to undergo no measurable exchange in methanol-d_4 in the absence of base after approximately 12 h.

Rates of $H_{3,4}$ exchange in **1**–**4** were slower than for $H_{2,5}$ and were followed readily by ^1H NMR. Values for k_{obsd} are shown in Table I. Examination of rates over at least a 5-fold KOH concentration range showed a linear dependence of the rate on KOH concentration (eq 4). Values of the second-order rate constant, *k* are shown in Table II.

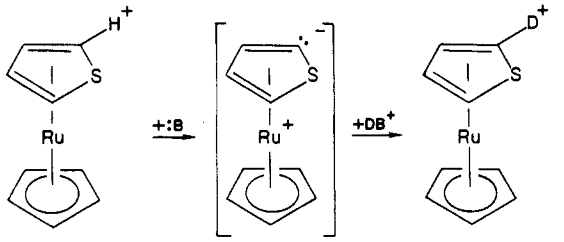
Rates of deuterium incorporation into the methyl substituents in **2**, **3**, and **4** were also monitored. Only small amounts of CH_3 exchange (approximately 10%) were seen in the ^1H NMR spectra of **2** in the presence of 0.050 M KOH during a 4-h period and **3** in the presence of 0.050 M KOH during 6 h. In a study of complex **2**, over 15 h with 0.040 M KOH, splitting of the methyl singlet due to coupling of the methyl hydrogens with incorporated deuterium was observed. Still, only 30% of the methyl hydrogens were exchanged. The rate constant, *k*, for methyl exchange (Table II) was estimated from a first-order plot of data from this run. For complex **4**, with the 2,5-DMT ligand, less than 10% of the methyl hydrogens were exchanged in the presence of 0.2 M KOH over a period of 4 h. The estimated rate constant k_{obsd} for this run is in Table II.

Chart I. Rate Constants 10^3k (M^{-1} s^{-1}) for Deuterium Exchange in Complexes 1–4



Discussion

Mechanism of Deuterium Exchange in CpRu(thiophene)$^+$ Complexes. The rate law (eq 4) with a first-order dependence on the OH^- concentration suggests that all of the exchange reactions occur by a mechanism in which OH^- removes H^+ from the thiophene in the slow step; this is followed by rapid deuterium (D^+) transfer to the intermediate from the solvent to give the deuteriated product, e.g., eq 5. The rates of exchange of the different types of hydrogen in complexes **1**–**4** decrease in the order $H_{2,5} \gg H_{3,4} > CH_3$ (Chart I). It is not entirely clear why $H_{2,5}$ are so easily deprotonated. Perhaps the lone pair resulting from deprotonation is stabilized by the vacant d orbitals of the adjacent sulfur, as has been suggested for sulfur-stabilized carbanions.[13] It should also be noted that the α-hydrogens in free thiophene are relatively more acidic than those in the β-positions.[14] Thus, the 2,5-hydrogens can be deprotonated with lithium alkyls much more readily than the 3,4.[15] Metalation of the 2,5-positions in $Cr(CO)_3$(thiophene)[16] with lithium alkyls also occurs. The observed rates of exchange for H_3 and H_4 in **1**, **2**, and **4** and H_4 in **3** decrease in the order **1** > **2** > **3** > **4**. Presumably, the increased electron density donated by substituent methyl groups in **2**, **3**, and **4** reduce the rate of proton abstraction by OH^- (eq 3) by making the exchanging protons less acidic. For **2**, where it might be expected that rates of exchange for H_3 and H_4 might differ,



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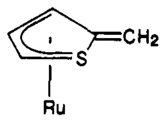
exchange of each of the protons was followed separately. First-order plots of H_3 differed from those for H_4 by no more than 5%. It is interesting that β-hydrogen exchange for **3** is a factor of 2 slower than that for **2**, presumably due to some electronic effect of the methyl at position 3.

The exchange of protons in the CH_3 groups is very slow. Deprotonation of the CH_3 groups in **2**, **3**, and **4** would give exocylic methylene complexes e.g.



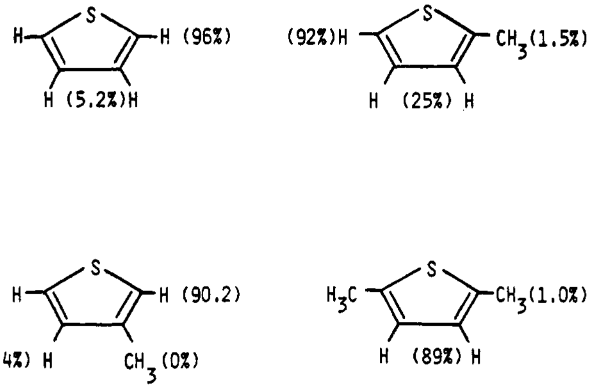
Related complexes have been obtained by deprotonation of CH_3 groups in π-methylbenzene complexes of Ru, Fe, and Mn.[17] In the present systems, it appears that such exocylic methylene complexes are not sufficiently stable to promote rapid deuterium exchange into the CH_3 groups.

Deuterium Isotope Effect in the Exchange of [CpRu(η-thiophene)]PF_6. For an exchange mechanism (eq 5) involving rate-determining C–H deprotonation by OH^-, one would expect the exchange in the deuterio analogue CpRu(η-thiophene-d_4)$^+$ to be 5–7 times slower than in that in **1**, as is found in other base-catalyzed deprotonation reactions.[19] To determine the isotope effect in this system, the appearance of the η-thiophene proton signals of **1** in a solution of CpRu(η-thiophene-d_4)$^+$ and 0.05 M KOH in CH_3OH was followed. The signals for $H_{2,5}$ had grown in completely within 10 min of starting the reaction; thus, this exchange was too fast to be studied, as was also the case for the exchange of **1** with CD_3OD.

No detectable exchange of $H_{3,4}$ in CpRu(η-thiophene-d_4)$^+$ was observed by ^1H NMR after 40 min. After 4 h, weak $H_{3,4}$ signals of **1** were apparent but decomposition of the complex was indicated by darkening of the reaction mixture and by the appearance of free thiophene in the spectrum. Because of this decomposition and the possibility that OH^- was consumed in the decomposition reaction, the rate of exchange was estimated after 40 min when no decomposition was evident. At this time, no more than 15% of **1** could have formed; this gives an upper limit for the second-order rate constant k_D of 1.4×10^{-3} M^{-1} s^{-1}. This constant together with that (k_H) for the exchange of **1** gives a k_H/k_D ratio of at least $(8.0 \times 10^{-3}\ M^{-1}\ s^{-1})/(1.4 \times 10^{-3}\ M^{-1}\ s^{-1}) = 5.7$, a deuterium isotope effect which is consistent with the mechanism in eq 5 involving rate-determining deprotonation.

Relevance to Catalytic Hydrodesulfurization. In deuterium exchange studies of thiophene over HDS catalysts (eq 1), exchange is seen primarily at the 2- and 5-positions with only small amounts of exchange in positions β to the sulfur.[5] Relatively few deuterium exchange studies have been reported for substituted thiophenes. Smith et al.[5a] investigated exchange of thiophene, 2-MT, 3-MT, and 2,5-DMT over supported molybdenum catalysts at 200 °C. They report the amounts of mono- (d_1), di- (d_2), tri- (d_3), and tetra- (d_4) deuteriated thiophenes obtained under the same conditions. In all cases, the amounts of nondeuteriated thiophenes (d_0) were small. Using their data, we calculated the amounts of deuterium incorporated at each of the three types of positions on the ring, α, β, and CH_3. Two assumptions were made in these calculations. First, the α-hydrogens of thiophenes exchange before the β-hydrogens. This assumption is supported by several studies. Smith et al.[5a] in their exchange studies of thiophene on supported catalysts, Mo/Al_2O_3 and $CoMo/Al_2O_3$ at 200 °C, found by NMR analysis that positions 2 and 5 contained most of the deuterium. For 2-methylthiophene and 3-methylthiophene mainly 5-deuterio-2-methylthiophene and 2,5-dideuterio-3-methylthiophene were formed.[5a] Cowley[5d] also found by deuterium NMR that exchange occurs primarily at the α-positions. Kieran and Kemball analyzed thiophene exchange over MoS_2 at 240 °C by ^1H NMR.[18] Greater than 95% of the exchanged hydrogens were found to be α-hydrogens. Second, it is assumed that β-hydrogens of the ring exchange prior to those in the methyl groups.[5a] Smith et al.[5a] as well as Cowley[5d] see only minor amounts of deuterium in α-methyl groups and none in β-methyls, e.g., in 3-methylthiophene.

Chart II. Percent Deuteriation of Thiophene, 2-Methylthiophene, 3-Methylthiophene, and 2,5-Dimethylthiophene over Mo/Al$_2$O$_3$ at 200 °C



Using these assumptions, we calculate the percent hydrogen at each position that has been substituted by deuterium in studies over a molybdenum/Al_2O_3 catalyst at 200 °C[5a] (Chart II). For thiophene, 96% of all the hydrogen at $H_{2,5}$ was substituted with deuterium, while only 5.2% of the β-hydrogens exchanged. For 2-methylthiophene, most of the α-hydrogen at C_5 exchanged, but a very small fraction of the methyl hydrogens did. The results in Chart II indicate the relative amounts of exchange over the Mo/Al_2O_3 catalyst as $H_{2,5} > H_{3,4} > CH_3$. For the model complexes **1**–**4**, the rates of exchange (Chart I) for the three types of hydrogens decrease in the same order: $H_{2,5} > H_{3,4} > CH_3$. Although $H_{2,5}$ exchange more rapidly than $H_{3,4}$ both in complexes **1**–**4** and on the catalyst, the differences between these rates are much larger in the complexes. It is not clear why this is true and to what extent this difference is affected by the metal and its other ligands.

If one compares just the monomethylthiophenes, exchange of H_4 in 3-MT is slower (or less extensive) than $H_{3,4}$ in 2-MT in the complexes (Chart I) and also over the catalyst (Chart II). Although it is not clear why a 3-methyl group slows exchange at H_4 more than a 2-methyl group, the effect is the same in the complexes and on the catalyst.

The same trend in rates of deuterium exchange in complexes **1**–**4** and on HDS catalysts suggests that thiophene is *π-bonded to a metal site (e.g., Mo) on the catalyst.* A basic site, e.g., S^{2-} or O^{2-} (on the alumina support), could abstract a proton; deuteriation by an acidic SD^- or OD^- would give the deuteriated product. Both SH^- and S^{2-} groups are present on HDS catalysts.[20] In earlier studies,

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[19] (a) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 2nd ed.; Harper and Row: New York, 1981; Chapter 2. (b) Melander, L. *Isotope Effects on Reaction Rates*; Roland Press: New York, 1960; Chapter 4.

Spies and Angelici[8c] showed that Al_2O_3 deuteriated with D_2O was capable of exchanging with $H_{2,5}$ in 1. The exchange was proposed to be catalyzed by basic oxygen groups on the Al_2O_3 surface.

Relative amounts of $H_{3,4}$ exchange in the differently substituted thiophenes over heterogeneous catalysts are different from the relative rates of exchange in the model complexes 1–4. That is, over HDS catalysts the amounts of $H_{3,4}$ exchange (Chart II) decrease in the order 2,5-DMT > 2-MT > 3-MT > thiophene,[5a,6a] whereas the rates of $H_{3,4}$ exchange in the complexes decrease as thiophene > 2-MT > 3-MT > 2,5-DMT. This difference in trends may be explained by considering that over the catalyst the extent of exchange is dependent not only on the rate of exchange of the absorbed thiophene but also on the amount of the thiophene that is adsorbed. In fact, competitive adsorption studies by Zdrazil[6,21] on CoMo/Al_2O_3 give relative adsorption capacities in the order 2,5-DMT (2.5) > 3-MT (~1.7) ≥ 2-MT (1.6) > thiophene (1.0).[22] Thus, the thiophenes with the most methyl groups adsorb to the greatest extent and should therefore have the greatest opportunity to undergo deuterium exchange. And this is the order of exchange that is observed. Thus, the extent of adsorption is more important than the opposing trend which would suggest that the more methyl groups in a π-adsorbed thiophene, the slower its deuterium exchange.

While the model studies presented herein do not prove that deuterium exchange of thiophenes on HDS catalysts proceeds via a π-adsorbed thiophene intermediate, they do provide for the first time experimental results that account for the observed amounts of exchange in the various positions of thiophenes over HDS catalysts. The mechanism of exchange in the model system also suggests that basic sites on the catalyst surface are important in promoting the exchanges; presumably more basic supports than Al_2O_3 would increase the rates of exchange, a possibility that could be examined experimentally.

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Registry No. 1, 107799-36-0; 2, 107799-38-2; 3, 107799-40-6; 4, 107799-42-8; H_2, 1333-74-0; $CpRu(PPh_3)_2Cl$, 32993-05-8; 2-MT, 554-14-3; 2,5-DMT, 638-02-8; $[CpRu(\eta\text{-}C_6H_6)]PF_6$, 72812-91-0; $[CpRu(NCCH_3]_3PF_6$, 80049-61-2; $[CpRu(\eta\text{-}2\text{-}MT)]PF_6$, 107799-43-9; $[CpRu(\eta\text{-}C_6H_6)]BF_4$, 91753-79-6; $[CpRu(NCCH_3)_3]BF_4$, 107799-44-0; $[CpRu(\eta\text{-thiophene-}d_4)]PF_6$, 107819-47-6; D_2, 7782-39-0.

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(21) Adsorption studies were accomplished by pulsing the thiophenes and mixtures of thiophenes through a column packed with CoMo/Al_2O_3 catalyst at 350 °C under He. Relative adsorptivities were obtained from retention times. See ref 6.

(22) It should be noted that the thiophene adsorption sites in these studies need not be the same sites where deuterium exchange occurs. Thus, the adsorption results may not be related to the deuterium exchange process.

Synthesis, Structure, and Reactivity of the Thioformaldehyde Complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}H_2C{=}S)]^+PF_6^-$

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Reaction of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)({=}CH_2)]^+PF_6^-$ (**2**) and $S{=}PPh_3$ gives a 1:1 mixture of thioformaldehyde complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}H_2C{=}S)]^+PF_6^-$ (**1**) and ylide complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2PPh_3)]^+PF_6^-$ (**3**). However, reaction of **2** and cyclohexene sulfide gives **1** (85–95% after recrystallization). An X-ray structure of **1** (crystal data: monoclinic, $P2_1/c$; a = 9.688 (2) Å, b = 18.536 (4) Å, c = 14.895 (s) Å; β = 103.53 (2)°; Z = 4) shows that the $\eta^2\text{-}H_2C{=}S$ ligand adopts a conformation that has significant overlap of its π^* orbital with the rhenium fragment HOMO and its sulfur terminus syn to the PPh_3. Extended Hückel MO calculations on the model compound $[(\eta^5\text{-}C_5H_5)Re(NO)(PH_3)(\eta^2\text{-}H_2C{=}S)]^+$ predict a similar conformational energy minimum. Complex **1** is stable in CD_3CN (41 h, 51 °C) but rapidly reacts with PPh_3 (2 equiv) to give **3** (95%) and $S{=}PPh_3$ (88%). Reaction of **1** and $NaBH_3CN$ gives thiomethyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(SCH_3)$ (**5**, 85% after recrystallization). The reactivity of **1** is compared to that of formaldehyde complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}H_2C{=}O)]^+PF_6^-$, and the mechanisms of the above reactions are discussed.

Introduction

Thioformaldehyde is the parent member of a rare and unstable class of molecules, thioaldehydes.[2] Thioformaldehyde has been spectroscopically characterized in the gas phase[3] and is found in interstellar space.[4] It has also been the subject of numerous theoretical studies.[5] How-

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