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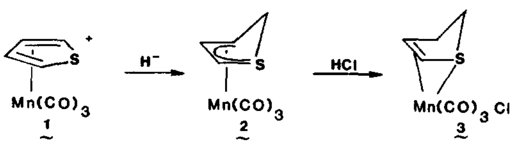
Studies of the Mechanism of Thiophene Hydrodesulfurization: Conversion of 2,3- and 2,5-Dihydrothiophene and Model Organometallic Compounds

Catalytic hydrodesulfurization (HDS), the process by which organically bound sulfur is removed from crude oils, is one of the largest-scale chemical processes practiced in the world (*1–3*). Thiophene is typical of the organosulfur compounds found in petroleum, and considerable effort has been directed toward investigating the mechanism for thiophene hydrodesulfurization (*4*). Recently, we have reported new kinetic information involving the HDS of thiophene, 2,3- and 2,5- dihydrothiophenes, and tetrahydrothiophene (*5*). These studies were performed with both Re/γ-Al_2O_3 and Mo/γ-Al_2O_3 catalysts using a flow microreactor system; in particular, rhenium studies provided new information data concerning reaction intermediates. We have also been able to prepare and characterize thiophene-related organometallic compounds which serve as plausible models for bonding and conversion on catalytic surfaces. The combination of these studies has led to new insights concerning alternate mechanistic pathways for thiophene HDS.

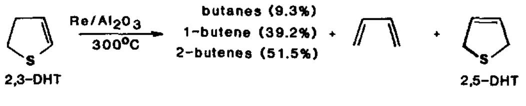
As a model for thiophene that is π-bonded to the catalyst surface, $[Mn(CO)_3(\eta\text{-thiophene})]SO_3CF_3$, **1**, was reacted with the metal hydrides $PPN[HFe(CO)_4]$ and $PPN[HW(CO)_5]$ (*6*):



(1)

These compounds represent hydride functionalities such as those proposed to exist on HDS catalyst surfaces (*7–9*). The neutral adduct $Mn(CO)_3(\eta\text{-thiophene} \cdot H)$, **2**, was formed. Adduct **2** reacted with strong acids such as HCl [a model for acidic surface SH sites (*10, 11*)] to give complex **3** with a 2,3-dihydrothiophene (2,3-DHT) ligand. Based on these model studies, 2,3-DHT was proposed (*6*) as a possible intermediate for thiophene HDS, in agreement with other suggestions that partial or complete hydrogenation of the thiophene ring occurs before the sulfur is removed (*8, 12–14*). However, if 2,3-DHT is an intermediate for thiophene HDS, it must undergo desulfurization much more rapidly than thiophene because 2,3-DHT has never been reported as a product of thiophene HDS. In reactor studies at 400°C using the 5% Re/γ-Al_2O_3 catalyst, only 23.2% of the thiophene reacted, whereas 2,3-DHT was completely converted (*15*). It is noteworthy that the C_4 hydrocarbon product distributions are very similar for thiophene and 2,3-DHT under these conditions; this is consistent with at least a portion of the thiophene being converted through a 2,3-DHT intermediate.

For reactor runs performed at 300°C, the C_4 hydrocarbon product distributions were dissimilar for thiophene and 2,3-DHT feeds. Furthermore, the products of the 2,3-DHT reaction contained butadiene (10.7%) and 2,5-DHT (11.7%), as well as thiophene (14.3%) and tetrahydrothiophene (54.8%) [and the C_4 hydrocarbons (8.5%)]:



(2)

The formation of butadiene and 2,5-DHT

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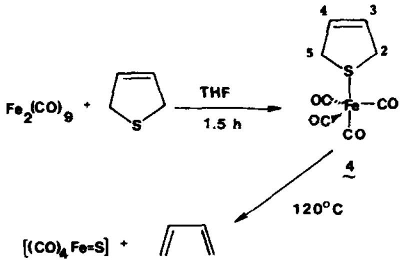
suggests that desulfurization might occur by isomerization of 2,3-DHT to 2,5-DHT, leading to the elimination of sulfur from 2,5-DHT to give butadiene. This proposal is supported by other 2,5-DHT (*16*) HDS reactor studies at 300°C where more than 60% of the desulfurized product was butadiene.

When 2,5-DHT was reacted with D_2 at 300°C using the Re/γ-Al_2O_3 catalyst, 65% of the butadiene product contained no deuterium. This suggests that 2,5-DHT eliminates butadiene directly, rather than first isomerizing to 2,3-DHT. Butadiene formation is likely to occur when the 2,5-DHT is coordinated via the sulfur to a metal site on the catalyst (*17–19*). We explored the possibility that this reaction would take place in a simple transition metal complex. The room temperature reaction of $Fe_2(CO)_9$ with 2,5-DHT in dry tetrahydrofuran (THF) produced $(CO)_4Fe$(2,5-DHT), **4**, which was isolated as an unstable red-brown oil:



(3)

The following spectroscopic results establish the composition and structure of **4** as shown in Eq. (3): ^1H NMR (d_6-acetone): δ 5.99 (2H, s, $H_{3,4}$), 4.01 (4H, s, $H_{2,5}$). ^{13}C NMR (d_6-acetone): δ 127.64 ($C_{3,4}$), 52.87 ($C_{2,5}$). EIMS: *m/e* 254 (parent ion = M^+), 226 (M^+-CO), 198 (M^+-2CO), 170 (M^+-3CO), 86 (DHT^+) base peak. IR (pentane): 2045 w, 1965 m, 1939 s. A small amount of **4** was heated in an evacuated NMR tube at 120°C for 10 min, giving a black solid. The tube was cooled in an ice bath, and $CDCl_3$ was added by syringe; the ^1H NMR spectrum was then obtained. Resonances for only butadiene (~30%) and free 2,5-DHT (~70%) were observed. The formation of butadiene was confirmed by gas chromatographic–mass spectrometric analysis of the gaseous decomposition products. The initial inorganic product of the reaction would presumably be $Fe(CO)_4({=}S)$; however, since only an insoluble black solid (presumably FeS) was observed, the putative Fe$(CO)_4({=}S)$ intermediate apparently decomposes rapidly at 120°C with a loss of CO. Regardless of the inorganic products, metal coordination to 2,5-DHT as shown in Eq. (3) giving rise to the elimination of butadiene is consistent with the reactor studies.

The combined results of the reactor studies and the model organometallic compound experiments suggest an overall mechanistic pathway for thiophene HDS as

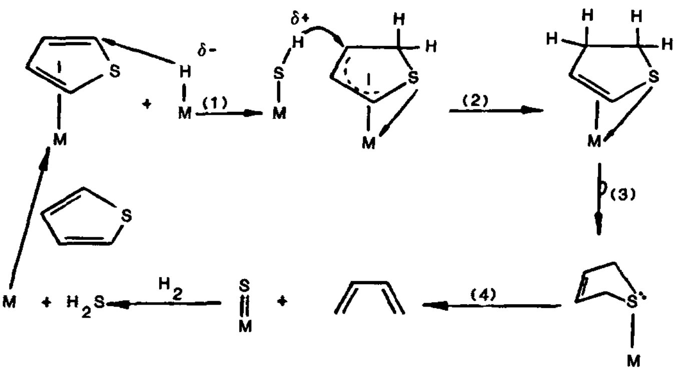


FIG. 1. Proposed mechanistic pathway for thiophene HDS via dihydrothiophene intermediates.

presented in Fig. 1. This pathway involves π-coordination of the thiophene to a metal site, surface hydride transfer to the 2-position of thiophene, and H^+ addition from an SH group to the 3-position. [The actual nature of these acid sites has not been completely determined. Some evidence using infrared spectroscopy of adsorbed NH_3 suggests that Brønsted acid sites may exist predominantly on the alumina surface (*20*).] It is also possible that two hydrogen atoms (rather than H^- and H^+) may transfer in steps (1) and (2) to produce 2,3-DHT as an intermediate. This 2,3-DHT may be coordinated via the sulfur and olefinic bond as shown or only via the sulfur (*17, 18*). After isomerization of 2,3-DHT to 2,5-DHT, butadiene is eliminated, leaving a surface sulfide which could be removed as H_2S upon reaction with hydrogen. The butadiene would be hydrogenated to the observed mixture of C_4 hydrocarbon products.

These studies are not offered as proof of the dominant occurrence of this pathway for thiophene HDS. However, this comprehensive mechanism, which is based on kinetic studies using model HDS catalysts and on the synthesis and characterization of relevant transition metal complexes, is offered as a plausible route for thiophene HDS.

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NANCY N. SAUER*
ERIC J. MARKEL†
GLENN L. SCHRADER†
ROBERT J. ANGELICI*

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

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