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Hydrodesulfurization of dibenzothiophene and its hydrogenated intermediates over sulfided Mo/γ-Al_2O_3

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ABSTRACT

Two intermediates of dibenzothiophene (DBT)—tetrahydro-DBT (THDBT) and hexahydro-DBT (HHDBT)—were synthesized, and their hydrodesulfurization (HDS) mechanism was investigated over Mo/γ-Al_2O_3 at 300–340 °C and 5 MPa in the absence and presence of H_2S and 2-methylpiperidine. The rate constants of all steps in the kinetic network of the HDS of DBT were measured. THDBT underwent desulfurization by hydrogenolysis to 1-phenylcyclohexene, followed by hydrogenation to phenylcyclohexane. The desulfurization of HHDBT occurred by hydrogenolysis of the aryl C–S bond and then cleavage of the cycloalkyl C–S bond of the resulting thiol by elimination to 1-phenylcyclohexene and by hydrogenolysis to phenylcyclohexane. H_2S strongly inhibited the desulfurization of all three molecules but did not inhibit (de)hydrogenation. 2-Methylpiperidine also had a strong inhibitory effect, especially on (de)hydrogenation and, to a lesser extent, on desulfurization. The order of the inhibition of DBT, THDBT, and HHDBT was explained by the adsorption constants of these three molecules.

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1. Introduction

Hydrodesulfurization (HDS) is the removal of sulfur atoms from sulfur-containing molecules in oil feed stocks by hydrogenation of the sulfur to hydrogen sulfide. Current legislation that has been or soon will be enacted in many parts of the world requires very low levels of sulfur in fuels. Because of the urgent need to lower these sulfur levels, improvements in the industrial HDS process are needed. This requires better understanding of the reaction mechanisms of various sulfur compounds. Dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (DMDBT) are the most refractory sulfur-containing molecules in gasoil [1–6]. Consequently, they are often used as model molecules, and their HDS has been studied in depth.

Extensive research on the HDS reaction mechanisms over metal sulfide catalysts has shown that DBT and DMDBT undergo HDS by two reaction pathways: direct desulfurization (DDS) and hydrogenation (HYD). Scheme 1 represents these pathways for the HDS of DBT. In the DDS pathway, the C–S bonds of the reactant molecule are broken by hydrogenolysis [7–9] or by elimination through a dihydro intermediate [10–12], leading to the formation of biphenyl (BP). In the HYD pathway, the reactant molecule is first hydrogenated to tetrahydro- (TH-), hexahydro- (HH-), and dodecahydro- (DH-) intermediates, and the sulfur atom is then removed to form cyclohexylbenzene (phenylcyclohexane; CHB) and bicyclohexyl (BCH). Due to the inhibitory effect of the neighboring methyl groups on the σ-bonding of sulfur to the catalytic sites, the HDS of DMDBT occurs mainly through the HYD pathway, but DDS dominates the HDS of DBT [4,12–15]. Therefore, the HDS of DMDBT through the HYD pathway is attracting increasing attention. It has been suggested that the catalyst must be sufficiently active in hydrogenation to hydrogenate DMDBT to its hydrogenated intermediates [16]. Nevertheless, the sulfur in the hydrogenated intermediates must be removed in the HYD pathway as well. How C–S bond breaking in these intermediates occurs remains an open question, because most studies to date have focused on DMDBT itself. The synthesis of the TH and HH intermediates has enabled the in-depth study of the HDS schemes of DBT and DMDBT and determination of the rates of all reaction steps over different catalysts [16,17]. Li et al. [17] suggested that the ring-opening of HH- and DH-DMDBT occurs through hydrogenolysis of the C–S bond; however, whether C–S bond breaking in TH-DMDBT occured remained unclear due to the rapid interconversion of TH-DMDBT and HH-DMDBT and their slow desulfurization reaction.

To gain further insight into the HDS mechanism, we studied the HDS of the hydrogenated intermediates of DBT. For DBT, the ratio of the rates of the desulfurization and the interconversion of THDBT and HHDBT should be larger than the corresponding ratio for the intermediates of DMDBT, because there is no hindrance of desulfurization by the methyl groups and no electron-donating effect on hydrogenation. Furthermore, preparing sufficient amounts of THDBT and HHDBT for a detailed study is easy. We investigated

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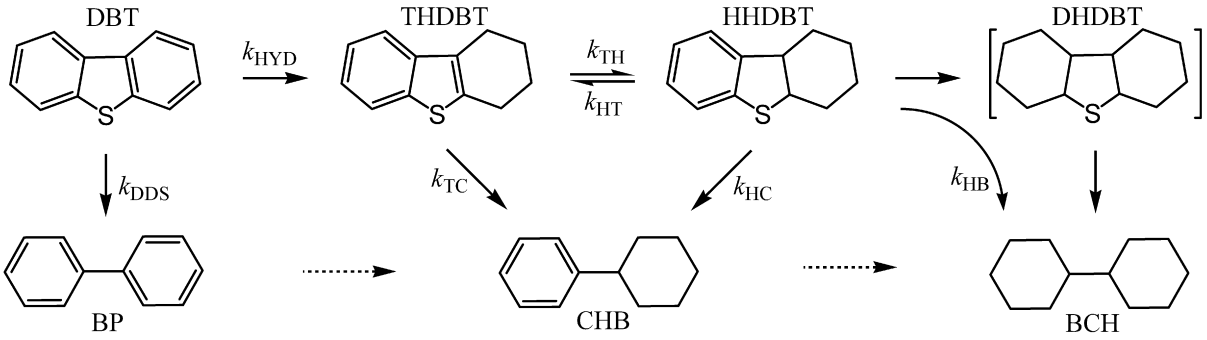
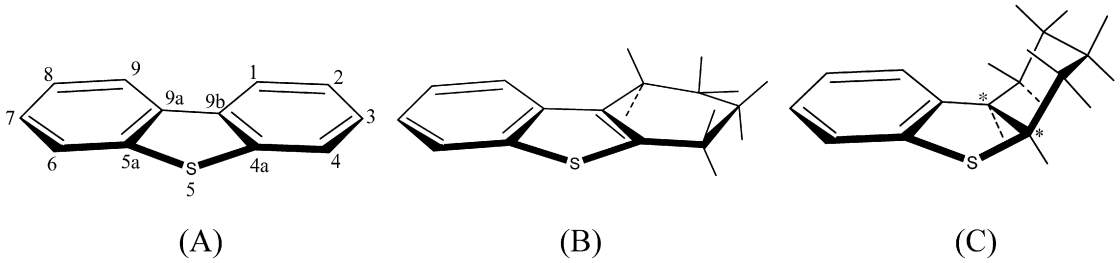


Scheme 1. Reaction network of the HDS of DBT.



Scheme 2. Conformation structure of (A) dibenzothiophene (DBT), (B) 1,2,3,4-tetrahydro-dibenzothiophene (THDBT), (C) 4a,9b-*cis*-1,2,3,4,4a,9b-hexahydro-dibenzothiophene (HHDBT) with chiral carbon atoms indicated by an asterisk.

the HDS of DBT, THDBT, and HHDBT at 300–340 °C and 5.0 MPa in the presence and absence of H_2S and a nitrogen-containing compound over sulfided Mo/γ-Al_2O_3. Our goal was to determine whether THDBT and HHDBT undergo desulfurization, how desulfurization occurs, and how fast these reactions are. We also investigated the influence of the H_2S, nitrogen-containing compound, and temperature on the HDS of the two molecules.

2. Experimental

The MoS_2/γ-Al_2O_3 catalyst used in this work contained 8 wt% Mo and was prepared by incipient wetness impregnation of γ-Al_2O_3 (Condea, pore volume 0.5 cm^3/g, specific surface area 230 m^2/g). The catalyst was crushed and sieved to a 230-mesh (<0.063 mm) particle size. Further details of the catalyst preparation can be found in [17].

The catalytic reactions were carried out in continuous mode in a heated fixed-bed inconel reactor, filled with 0.05 g catalyst diluted with 8 g SiC to achieve plug-flow conditions. The catalyst was sulfided in situ with a mixture of 10% H_2S in H_2 (50 ml/min) at 400 °C and 1.0 MPa for 4 h. After sulfidation, the pressure was increased to 5.0 MPa, the temperature was decreased to reaction temperature, and the liquid reactant was fed to the reactor by means of a high-pressure pump. Most of the HDS and hydrogenation experiments were performed at 300 °C; some experiments were carried out at 340 °C to study the influence of temperature. The gas-phase feed in most of the experiments consisted of 1 kPa of reactant (DBT, THDBT, or HHDBT, 0.5 and 3 kPa in some cases), 130 kPa toluene (as solvent), 8 kPa dodecane (as a GC reference), 0 or 35 kPa H_2S, and ~4.8 MPa of H_2. 2-Methylpiperidine (MPi, 0.5, 1, and 1.5 kPa) was added to the feed in some of the experiments to slow down the reaction and to study the influence of nitrogen-containing compounds. The conversion of MPi at 300 °C was not greater than 5% and 15% at the highest weight time in the absence and presence of H_2S, respectively. The HDS of 1 kPa thiophenol and cyclohexanethiol in the presence of 1 kPa DBT was investigated at 0 and 35 kPa H_2S and in the presence and absence of 1 kPa MPi (with octane as the solvent). Hydrogenation of the desulfurization intermediate cyclohexen-1-yl-benzene (1-phenylcyclohexene, 0.6 kPa) was investigated in the presence of 1 kPa THDBT and in the presence and absence of 1 kPa MPi. The reaction products were analyzed by offline gas chromatography with a Varian 3800 GC instrument equipped with a PTA-5 fused silica capillary column and a flame ionization detector. Mass spectrometry was used to identify the reaction products. The analysis was performed with an Agilent 6890 gas chromatograph equipped with an HP-5MS capillary column and an Agilent 5973 mass selective detector. Weight time was defined as the ratio of the catalyst weight to the molar flow to the reactor (1 g min/mol = 0.15 g h/l at 300 °C and 5.0 MPa). The weight time was changed by varying the flow rates of the liquid and the gaseous reactants while keeping their ratio constant. Every series of experiments over a fresh catalyst started with a stabilization period of at least one night (15 h) at the highest weight time. During 2 weeks of operation, almost no catalyst deactivation was observed. A single experiment lasted 12–24 h.

DBT (Acros), 2-methylpiperidine (Acros), thiophenol (Fluka), cyclohexanethiol (Aldrich), and cyclohexen-1-yl-benzene (Acros) were all used as purchased. THDBT (Scheme 2B) was synthesized in two steps according to the method of DiCesare et al. [18]. 2-Thiophenoxy-cyclohexanone, which was obtained from the reaction of 2-chlorocyclohexanone with thiophenol, was heated with polyphosphoric acid to form THDBT. HHDBT was made by hydrogenation of THDBT with zinc and trifluoroacetic acid at room temperature. Then 8 g of THDBT, 160 ml of trifluoroacetic acid, and 35 g of zinc powder were added to a flask equipped with a reflux cooler. The mixture was stirred with a magnetic stirrer for 4 days at room temperature, after which dichloromethane was added, and the residual zinc was filtered. The organic liquid was purified with water, sodium bicarbonate solution, and brine; dried with $MgSO_4$; evaporated under vacuum; and analyzed by GC-MS. The yield of HHDBT was >98%, and the product composition was 90% *cis*-HHDBT (Scheme 2C) and 10% *trans*-HHDBT. HHDBT has two chiral centers; thus, the hydrogen atoms on the carbon atoms at positions 4a and 9b can be in both *cis* and *trans* configuration, leading to *cis*-HHDBT and *trans*-HHDBT.

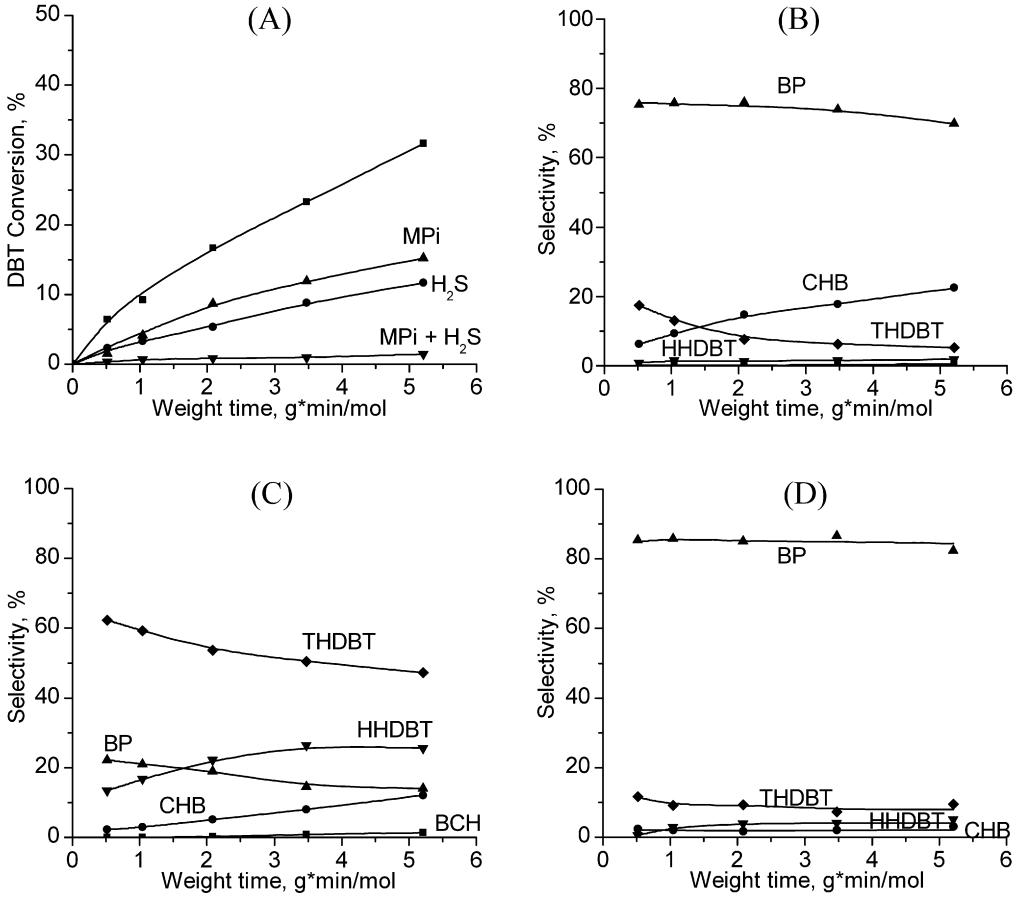


Fig. 1. HDS of DBT at 300 °C and 5.0 MPa. (A) Conversion of DBT in the absence of H_2S and MPi (■), in the presence of 35 kPa H_2S (●), in the presence of 1 kPa MPi (▲), and in the presence of both 35 kPa H_2S and 1 kPa MPi (▼). (B) Product selectivities in the absence of H_2S and MPi. (C) Product selectivities in the presence of 35 kPa H_2S. (D) Product selectivities in the presence of 1 kPa MPi.

3. Results

3.1. HDS of DBT

The HDS of 1 kPa DBT was first studied at 300 °C and 5.0 MPa in the absence and presence of H_2S and MPi. Fig. 1 gives the conversion of DBT and the product selectivities under different conditions. Five products were observed: biphenyl (BP), the product of the DDS pathway; THDBT and HHDBT, the intermediates of the HYD pathway; and cyclohexylbenzene (CHB) and bicyclohexyl (BCH), the final products of the HYD pathway (Scheme 1). The fully hydrogenated DHDBT intermediate was not detected. In the absence of H_2S and MPi, the DBT conversion was 32% at $\tau = 5.2$ g min/mol (Fig. 1A). The yield of the five products increased with weight time. BP was always the most abundant product; its selectivity was about 75% at low weight time and 70% at high weight time (Fig. 1B), indicating that the DDS pathway is much faster than the HYD pathway under these conditions. Slow hydrogenation of BP may explain the decrease is the selectivity of BP, because the increase in the selectivity of CHB with weight time was slightly higher than the decrease in the selectivity of THDBT. CHB was the second most abundant product at $\tau > 2.1$ g min/mol, indicating rapid desulfurization of the hydrogenated intermediates. The yield of BCH was very low, demonstrating that the complete hydrogenation of DBT was slow.

H_2S had a strong influence on the conversion of DBT. At 300 °C and 35 kPa H_2S, only 11% of DBT was converted at $\tau = 5.2$ g min/mol (Fig. 1A), almost three times less than that at 0 kPa H_2S. The decreased conversion was due mainly to the decreased formation of BP. The yield of BP at $\tau = 5.2$ g min/mol was 1.6%, almost 14 times lower than that at 0 kPa H_2S, indicating that H_2S strongly inhibited the DDS pathway. The sum of the yields of the other four compounds changed only slightly. However, the yield of CHB was about five times lower than that at 0 kPa H_2S due to inhibition of the desulfurization of THDBT and HHDBT by H_2S. Therefore, THDBT and HHDBT were major products (Fig. 1C). The results mentioned above and shown in Fig. 1 indicate that H_2S did not influence the hydrogenation of DBT but did shift HYD selectivity from the main final hydrocarbon product, CHB, to the S-containing intermediates THDBT and HHDBT due to decreased rates of THDBT and HHDBT desulfurization.

MPi also had a strong influence on DBT conversion. The conversion of DBT in the presence of 1 kPa MPi was about half that in the absence of MPi. The yield of BP was also about half, whereas the sum of the yields of the other four compounds was about one-third as great, indicating that MPi inhibited both pathways, especially the HYD pathway. As a result, BP represented 85% of the reaction products (Fig. 1D). In the presence of both 1 kPa MPi and 35 kPa H_2S, the conversion of DBT barely reached 1.5% at $\tau = 5.2$ g min/mol (Fig. 1A). The major products were BP and THDBT, with selectivities of 70% and 30%, respectively, which remained more or less constant with increasing weight time. Only small amounts of HHDBT and CHB were seen at high weight times.

The HDS of DBT at 300 °C and 35 kPa H_2S also was investigated at the higher initial partial pressure of 3 kPa DBT. The conversion of DBT was 1.7 times lower than that for 1 kPa DBT. The selectivity-time curve of the products (not shown) was almost the same as that for 1 kPa DBT, in agreement with the results of Egorova and

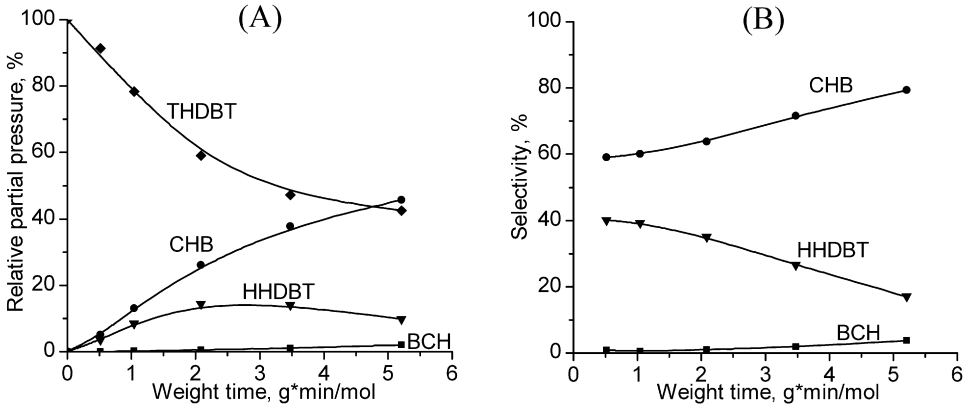


Fig. 2. Relative partial pressure of reactant and products (A) and product selectivities (B) of the HDS of THDBT as a function of weight time at 300 °C, 5.0 MPa, and 0 kPa H_2S.

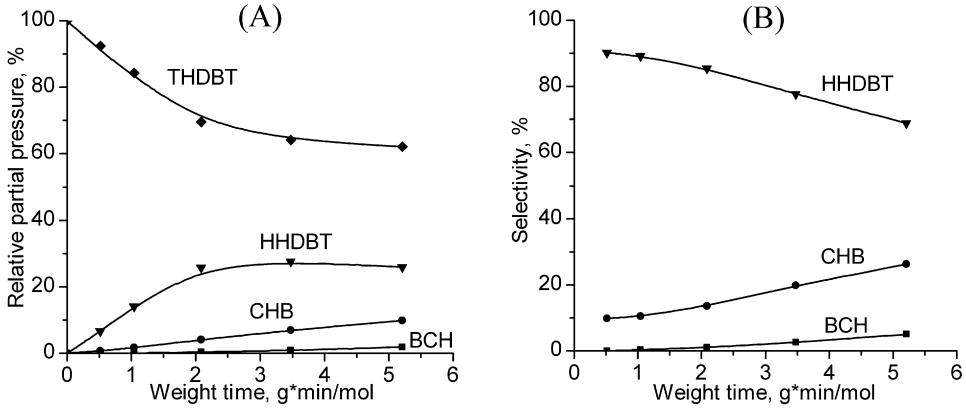


Fig. 3. Relative partial pressure of reactant and products (A) and product selectivities (B) of the HDS of THDBT as a function of weight time at 300 °C, 5.0 MPa, and 35 kPa H_2S.

Prins [15], who found decreasing conversion with increasing partial pressure of DBT from 0.1 to 3 kPa at 300 °C, 5.0 MPa, and 35 kPa H_2S over Mo/γ-Al_2O_3. The results indicate that the reaction of DBT at 300 °C and 35 kPa H_2S was between zero order and first order for an initial DBT partial pressure between 1 and 3 kPa.

The HDS of DBT in the absence and presence of H_2S and MPi also was studied at 340 °C. In the presence of 35 kPa H_2S, the conversion of DBT at 340 °C was about fourfold greater than that at 300 °C. The selectivity of BP was slightly higher and the selectivities of CHB and BCH were much higher at 340 °C, indicating that the desulfurization is more strongly promoted than hydrogenation at high temperatures. As was seen at 300 °C, MPi strongly inhibited both the HYD and DDS pathways.

3.2. HDS of THDBT

When the partially hydrogenated THDBT was used as the reactant, it converted rapidly to CHB and HHDBT at 300 °C and 0 kPa H_2S (Fig. 2A). Its conversion reached 58% at $\tau = 5.2$ g min/mol, which was about twice as high as that of DBT under the same conditions. CHB and HHDBT were primary products, because they had non-zero selectivities of 58 and 42%, respectively, at $\tau = 0$ (Fig. 2B). Hydrogenation and desulfurization were the main reactions of THDBT. CHB was the most abundant product, and its yield increased with weight time. The yield of HHDBT first increased and then decreased at $\tau > 2.1$ g min/mol, indicating that a further reaction (either dehydrogenation or desulfurization) of HHDBT occurred. The yield-time curves of THDBT and HHDBT suggest that these molecules have a tendency to reach equilibrium, with a THDBT/HHDBT ratio of 4.3 at $\tau = 5.2$ g min/mol. The yield of BCH was low, indicating that the further hydrogenation of HHDBT was slow.

H_2S strongly inhibited the desulfurization of THDBT. At 35 kPa H_2S, the yield of CHB at $\tau = 5.2$ g min/mol was about 4.5-fold lower than that at 0 kPa H_2S (Fig. 3A). H_2S slightly influenced the interconversion of THDBT and HHDBT, which tended to equilibrium, similar as that at 0 kPa H_2S; therefore, HHDBT was the most abundant product, with a yield greater than that at 0 kPa H_2S. The THDBT/HHDBT ratio was 2.4 at $\tau = 5.2$ g min/mol. CHB and HHDBT behaved as primary products. Extrapolation to $\tau = 0$ gave selectivities of 90% for HHDBT and of 10% for CHB (Fig. 3B).

MPi strongly inhibited both the desulfurization and hydrogenation of THDBT. At 0.5 kPa MPi, the conversion of THDBT was 14% at $\tau = 2.1$ g min/mol (Fig. 4A), almost threefold lower than that at 0 kPa MPi. At 1.0 kPa MPi, the conversion of THDBT was 11% at $\tau = 2.1$ g min/mol, almost fourfold lower than that at 0 kPa MPi. The THDBT/HHDBT ratios at 0.5 and 1 kPa MPi were 5.5 and 9.4 at $\tau = 5.2$ g min/mol, respectively, indicating that the two molecules were far from equilibrium. The selectivity of HHDBT at 1 kPa MPi was nearly constant with weight time (Fig. 4C), demonstrating that the further dehydrogenation and desulfurization of HHDBT were very slow. However, as we show in Section 3.3, HHDBT can react under these conditions. The very slow reaction of HHDBT under the present conditions is due to the inhibition by THDBT, the partial pressure of which was about fourfold greater than that of HHDBT at the highest weight time. The selectivity of HHDBT at zero weight time was slightly lower at 1 kPa MPi than at 0 kPa MPi, indicating that MPi inhibited the hydrogenation of THDBT somewhat more strongly than it inhibited desulfurization. Along with HHDBT and CHB, cyclohexen-1-yl-benzene (CHEB) was ob-

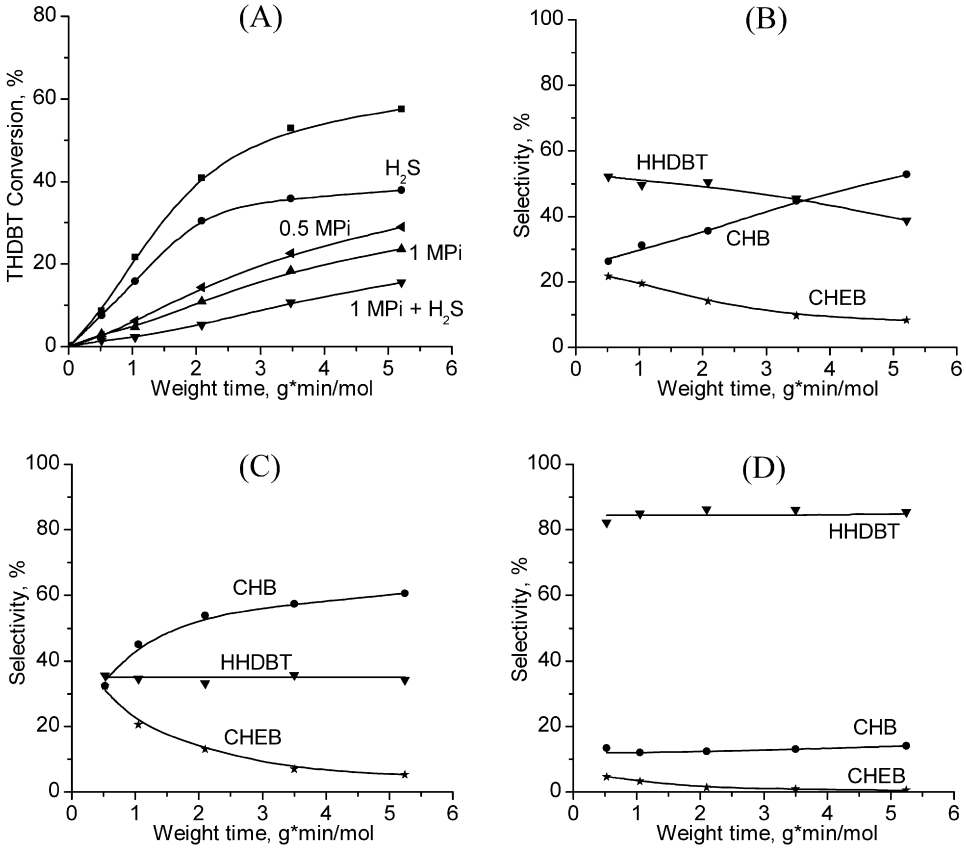


Fig. 4. HDS of THDBT at 300 °C and 5.0 MPa. (A) Conversion of THDBT in the absence of H_2S and MPi (■), in the presence of 35 kPa H_2S (●), in the presence of 0.5 kPa MPi (◀), in the presence of 1 kPa MPi (▲), and in the presence of both 35 kPa H_2S and 1 kPa MPi (▼). (B) Product selectivities in the presence of 0.5 kPa MPi. (C) Product selectivities in the presence of 1 kPa MPi. (D) Product selectivities in the presence of both 35 kPa H_2S and 1 kPa MPi.

served and behaved as a primary product, whereas CHB behaved as a secondary product in the presence of MPi (Figs. 4B and 4C), suggesting that the desulfurization of THDBT to CHB proceeded by the CHEB intermediate. MPi slowed the hydrogenation of CHEB to CHB; thus, CHEB could be observed and behaved as a primary product.

In the presence of both 1 kPa MPi and 35 kPa H_2S, the conversion of THDBT decreased further to 5% at $\tau = 2.1$ g min/mol (Fig. 4A). The major product was HHDBT, and its selectivity remained constant with increasing weight time (Fig. 4D). CHEB continued to behave as a primary product. Its selectivity was low because H_2S inhibited its formation and did not effect its hydrogenation.

The HDS of THDBT at 300 °C and 35 kPa H_2S also was investigated at the initial partial pressures of 0.5 and 3 kPa THDBT. The conversion of 0.5 kPa THDBT at $\tau = 2.1$ g min/mol was about 1.3-fold greater than that of 1 kPa THDBT, and that of 3 kPa THDBT was about 2.6-fold lower. The selectivities of HHDBT and CHB at zero weight time of the three reactions were nearly the same. The results indicate that the reaction of THDBT at 300 °C and 35 kPa H_2S was between first and zero order for a initial THDBT partial pressure between 0.5 and 3 kPa.

The HDS of THDBT in the absence and presence of H_2S and MPi also was studied at 340 °C (Fig. 5). In the absence of H_2S, the HDS of THDBT was extremely fast and reached 100% conversion at low weight time (not shown). In the presence of 35 kPa H_2S, the conversion of THDBT at $\tau = 2.1$ g min/mol was about twice as high at 340 °C as at 300 °C. A substantial amount of BCH was produced, indicating that the further hydrogenation of THDBT to HHDBT and then to DHDBT (which then quickly reacted to BCH) was promoted at high temperature. The selectivity of CHB was greater at 340 °C than at 300 °C (cf. Figs. 5B and 3B), proving that desulfurization was promoted over hydrogenation at high temperature, in agreement with the results of the HDS of DBT. HHDBT behaved as a primary product, and its selectivity decreased quickly with weight time due to the fast reaction of HHDBT to BCH. The selectivity of CHB decreased quickly with decreasing weight time. Furthermore, at 340 °C and in the presence of 1 kPa MPi, CHEB behaved as a primary product (Fig. 5C). Because of the higher temperature, the further reaction of HHDBT was not as slow as that at 300 °C in the presence of 1.0 kPa MPi, and thus its selectivity decreased with weight time. Even in the presence of both 1 kPa MPi and 35 kPa H_2S, the further reaction of HHDBT was substantial (Fig. 5D). As at 300 °C, MPi strongly inhibited both the hydrogenation and desulfurization of THDBT.

3.3. HDS of HHDBT

HHDBT was a very reactive component at 300 °C and 0 kPa H_2S (Fig. 6A). At $\tau = 2.1$ g min/mol, already 70% of HHDBT had converted to THDBT with a selectivity of 65%. THDBT forms by dehydrogenation of the reactant and acts as a primary product (Fig. 6B). It was the most abundant compound at $\tau < 3.5$ g min/mol, and its yield passed through a maximum, indicating that further reaction (i.e., desulfurization) occurred. The yield of CHB increased with weight time, and CHB was the most abundant product at the highest weight time. Because of its formation from HHDBT as well as THDBT, its selectivity increased with increasing weight time. The relative partial pressures of the reactant and products of the HDS of HHDBT at high weight times were very similar to those obtained in the HDS of THDBT (Fig. 2A). THDBT and HHDBT tended to equilibrium, with a THDBT/HHDBT ratio of 3.5 at $\tau = 5.2$ g min/mol. The yield of BCH was low, even when starting

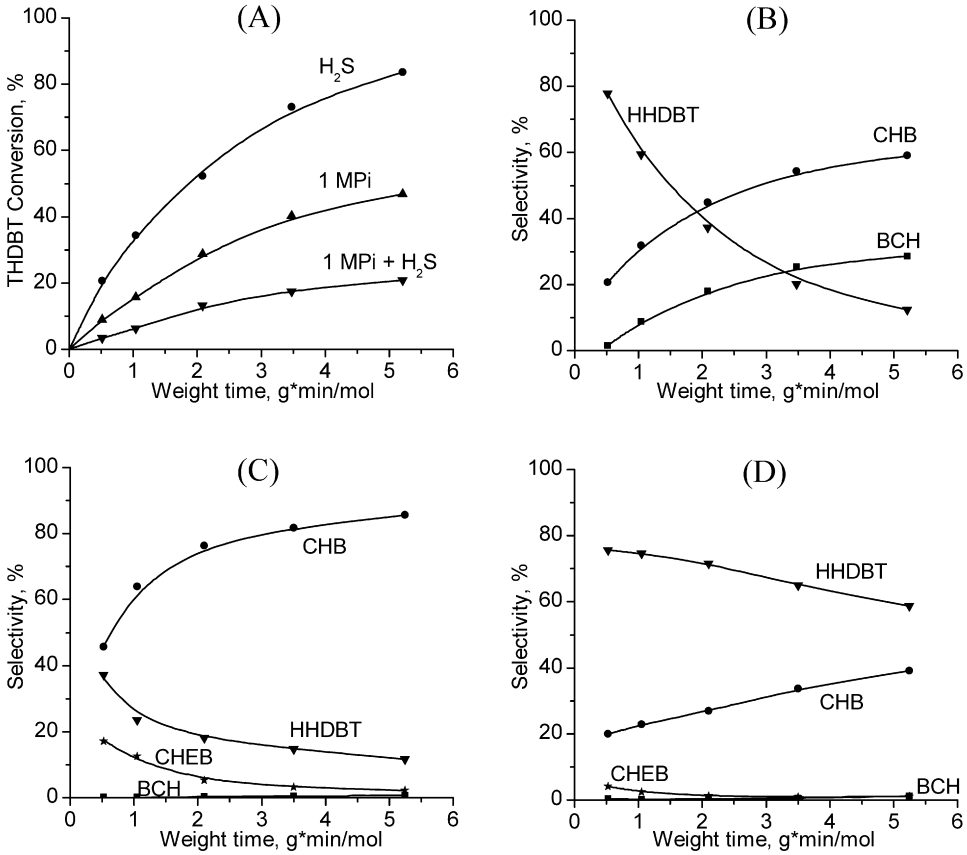


Fig. 5. HDS of THDBT at 340 °C and 5.0 MPa. (A) Conversion of THDBT in the presence of 35 kPa H_2S (●), in the presence of 1 kPa MPi (▲), and in the presence of both 35 kPa H_2S and 1 kPa MPi (▼). (B) Product selectivities in the presence of 35 kPa H_2S. (C) Product selectivities in the presence of 1 kPa MPi. (D) Product selectivities in the presence of both 35 kPa H_2S and 1 kPa MPi.

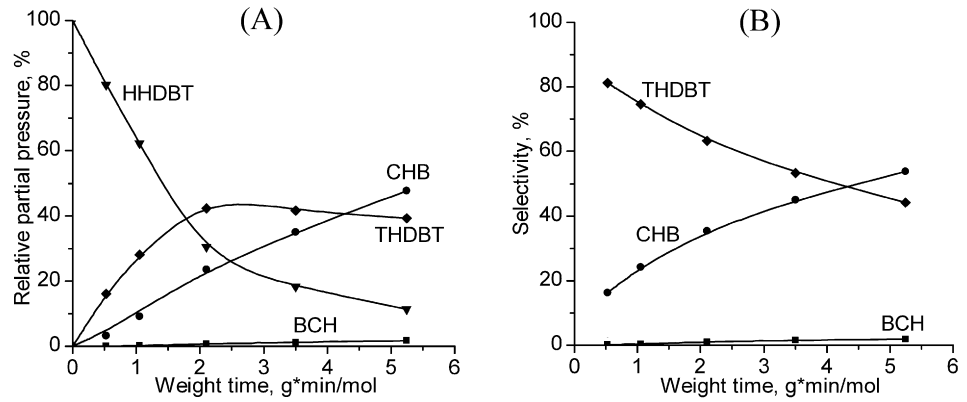


Fig. 6. Relative partial pressure of reactant and products (A) and product selectivities (B) of the HDS of HHDBT as a function of weight time at 300 °C, 5.0 MPa, and 0 kPa H_2S.

from HHDBT, demonstrating that further hydrogenation of HHDBT to DHDBT was slow.

H_2S strongly inhibited the desulfurization of HHDBT. In the presence of 35 kPa H_2S, a product distribution at high weight time (Fig. 7A) similar to that when starting from THDBT (Fig. 3A) was obtained. THDBT and CHB behaved as primary products. This again indicates that THDBT and HHDBT tended to equilibrium after some time and then simultaneously reacted further. Extrapolation to $\tau = 0$ gave 92% selectivity of HHDBT and 8% selectivity of CHB (Fig. 7B). The THDBT/HHDBT ratio was 1.9 at $\tau = 5.2$ g min/mol.

MPi strongly inhibited both the desulfurization and dehydrogenation of HHDBT (Fig. 8A). At 1 kPa MPi, the conversion of HHDBT was 10% at $\tau = 2.1$ g min/mol, almost sevenfold lower than that at 0 kPa MPi. The selectivity of THDBT at zero weight time was lower at 1 kPa MPi than at 0 kPa MPi, indicating that MPi inhibited the dehydrogenation of HHDBT more strongly than the desulfurization of HHDBT. The inhibitory effect of MPi on HDS was stronger for HHDBT than for THDBT. The selectivity of THDBT decreased with weight time, indicating that THDBT reacted further (Fig. 8B). Therefore, a reaction was performed at 1.5 kPa MPi. The conversion-time curve of HHDBT was nearly the same as that at 1.0 kPa MPi, but the selectivity of THDBT remained more or less constant with weight time (Fig. 8C). The THDBT/HHDBT ratio at $\tau = 5.2$ g min/mol was 0.13 at 1 kPa MPi and 0.12 at 1.5 kPa MPi, indicating strongly inhibited interconversion of THDBT and HHDBT by the nitrogen-containing compound. CHEB behaved as a primary

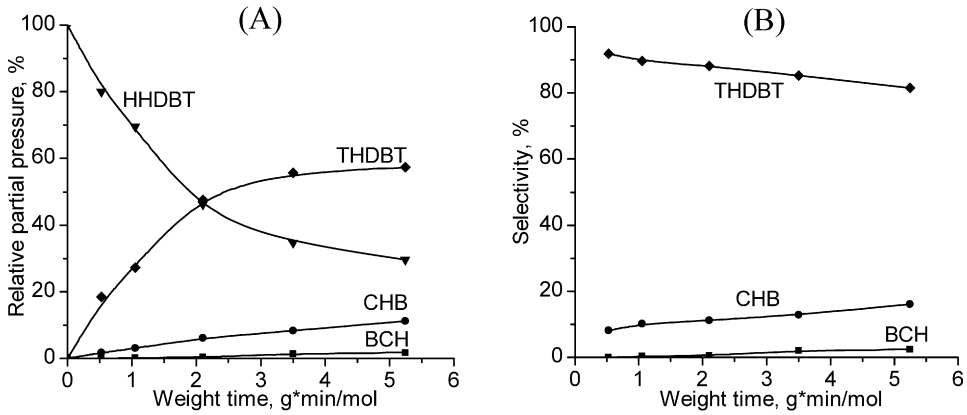


Fig. 7. Relative partial pressure of reactant and products (A) and product selectivities (B) of the HDS of HHDBT as a function of weight time at 300 °C, 5.0 MPa, and 35 kPa H_2S.

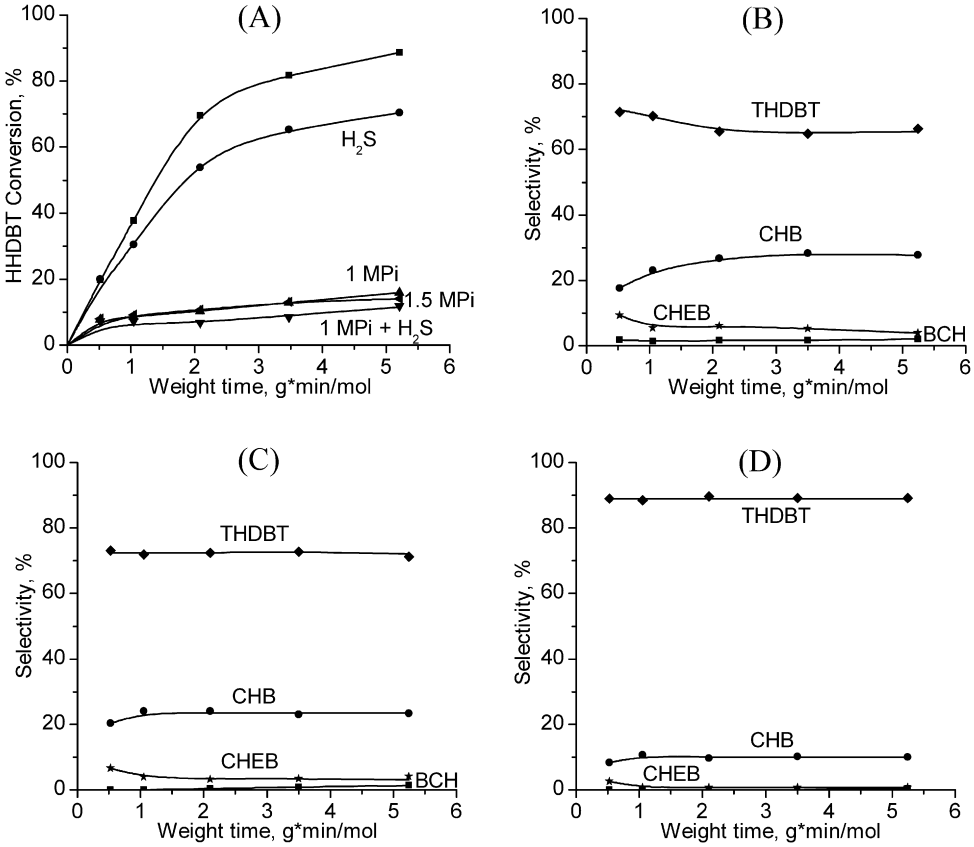


Fig. 8. HDS of HHDBT at 300 °C and 5.0 MPa. (A) Conversion of HHDBT in the absence of H_2S and MPi (■), in the presence of 35 kPa H_2S (●), in the presence of 1 kPa MPi (▲), in the presence of 1.5 kPa MPi (◀), and in the presence of both 35 kPa H_2S and 1 kPa MPi (▼). (B) Product selectivities in the presence of 1 kPa MPi. (C) Product selectivities in the presence of 1.5 kPa MPi. (D) Product selectivities in the presence of both 35 kPa H_2S and 1 kPa MPi.

product in the reaction at 1.0 and 1.5 kPa MPi (Figs. 8B and 8C); however, its selectivity was always very low and CHEB was not the only primary desulfurization product.

In the presence of both 1 kPa MPi and 35 kPa H_2S, the conversion of HHDBT decreased further to 7% at $\tau = 2.1$ g min/mol (Fig. 8A). The major product was THDBT, the selectivity of which remained constant with weight time (Fig. 8D). CHEB and CHB also behaved as primary products, and the selectivity of CHEB was very low.

The HDS of HHDBT at 300 °C and 35 kPa H_2S also was investigated starting with 3 kPa THDBT. The reaction profile was almost the same as that of 1 kPa HHDBT, indicating that the reaction of HHDBT was first order under these conditions.

At 340 °C, in the absence of H_2S, the HDS of HHDBT was extremely fast and reached 100% conversion at low weight time. In the presence of 35 kPa H_2S, the conversion of HHDBT reached 68% at $\tau = 0.5$ g min/mol, almost 3.5 times higher than that at 300 °C (cf. Figs. 7A and 9A). THDBT was the most abundant product at low weight time. The selectivity of CHB increased with weight time, and CHB was the most abundant product at high weight time. A substantial amount of BCH also was seen. The relative partial pressures of the reactant and products of the HDS of HHDBT at $\tau > 1$ g min/mol were very similar to those obtained in the HDS of THDBT at 340 °C, demonstrating the very fast interconversion of HHDBT and THDBT. The selectivity of CHB was slightly higher at 340 °C (Fig. 9B) than at 300 °C (Fig. 7B), indicating that desulfur-

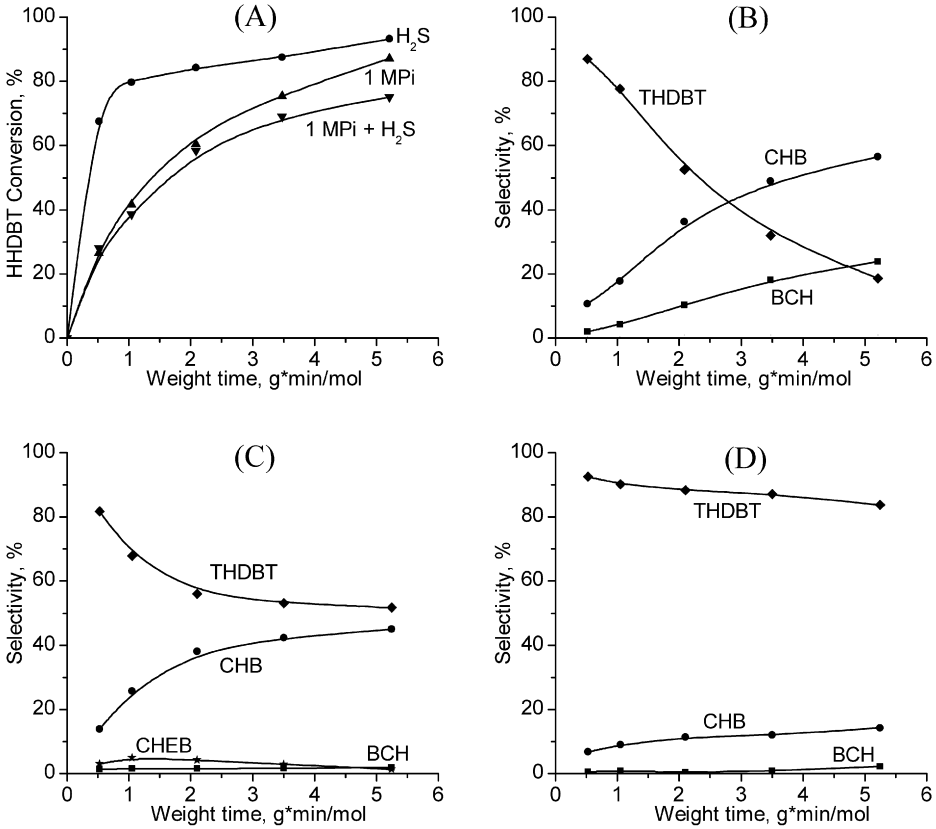


Fig. 9. HDS of HHDBT at 340 °C and 5.0 MPa. (A) Conversion of HHDBT in the presence of 35 kPa H_2S (●), in the presence of 1 kPa MPi (▲), and in the presence of both 35 kPa H_2S and 1 kPa MPi (▼). (B) Product selectivities in the presence of 35 kPa H_2S. (C) Product selectivities in the presence of 1 kPa MPi. (D) Product selectivities in the presence of both 35 kPa H_2S and 1 kPa MPi.

ization was more strongly promoted at high temperature. A substantial amount of BCH was produced, indicating that the further hydrogenation of HHDBT to DHDBT was fast at high temperature. This finding also explains the small increase in selectivity of CHB. THDBT behaved as a primary product, and its selectivity decreased rapidly with weight time. At 340 °C and in the presence of 1 kPa MPi, CHEB was produced, and its selectivity was low (Fig. 9C). Because of the high temperature, the further reaction of THDBT was fast in the presence of 1.0 kPa MPi, and its selectivity still decreased with weight time (Fig. 9C). Even when inhibited by both 1 kPa MPi and 35 kPa H_2S, the further reaction of THDBT was still reasonably fast (Fig. 9A). Similar as at 300 °C, MPi strongly inhibited both the hydrogenation and desulfurization of HHDBT.

3.4. HDS of thiophenol and cyclohexanethiol

Arylthiols have been proposed as intermediates after the first C–S bond cleavage of DBT and DMDBT [10,17,19]. But they have never been observed, and it is assumed that they react very rapidly. To check this assumption, we investigated the HDS of 1 kPa thiophenol and cyclohexanethiol under the conditions in our study in the presence of DBT. At 300 °C and 0 or 35 kPa H_2S in the presence of 1 kPa DBT, thiophenol reacted very fast and was converted completely to benzene at the lowest weight time. At 300 °C and 0 kPa H_2S in the presence of 1 kPa DBT, cyclohexanethiol also reacted very fast and was converted completely to cyclohexene and cyclohexane at the lowest weight time. The ratio of cyclohexene to cyclohexane was 8 at the lowest weight time and 2 at the highest weight time. At 35 kPa H_2S, cyclohexanethiol reacted slightly more slowly, but its conversion was always >96%. MPi further inhibited the reaction of cyclohexanethiol, and its conversion at the lowest weight time was 81% at 300 °C and 35 kPa H_2S in the presence of 1 kPa MPi. The ratio of cyclohexene to cyclohexane was 3 at the lowest weight time and 0.8 at the highest weight time. These results prove that the hydrodesulfurization of thiols was very fast under our reaction conditions.

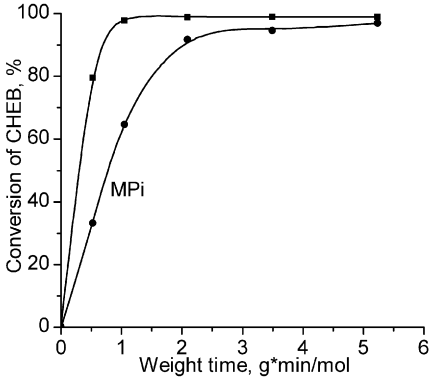
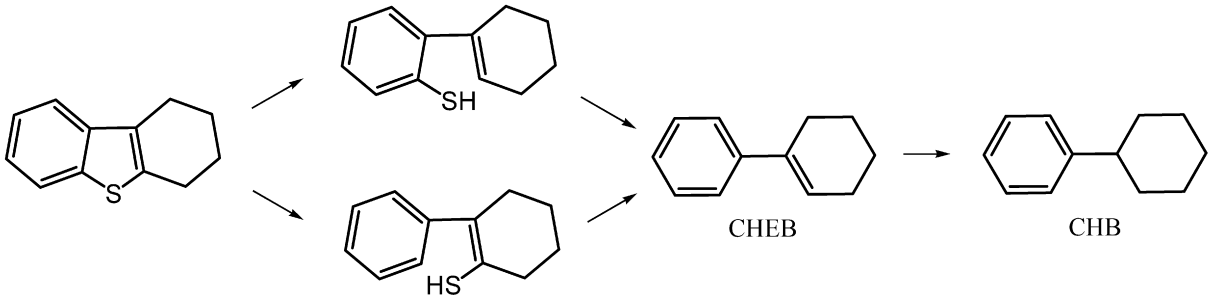


Fig. 10. Hydrogenation of CHEB to CHB at 300 °C, 5.0 MPa, and 0 kPa H_2S in the presence of 1 kPa THDBT and in the absence (■) and presence (●) of 1.0 kPa MPi.

3.5. Hydrogenation of CHEB

CHEB was observed in the desulfurization of THDBT and HHDBT in the presence of MPi and was considered an intermediate that was formed from the sulfur-containing compound and then hydrogenated to CHB. But it was not always present in the absence of MPi, likely due to the rapid hydrogenation to CHB. To prove this, the hydrogenation of 0.6 kPa CHEB in the presence of 1 kPa THDBT was studied at 300 °C and 0 kPa H_2S in the absence and presence of 1 kPa MPi (Fig. 10). The hydrogenation of CHEB in the absence of



Scheme 3. Possible reaction pathways in the desulfurization of THDBT.

MPi was fast. CHEB was converted to CHB and did not react further to BCH. Its conversion reached 80% at the lowest weight time and was >99% at $\tau > 1$ g min/mol. This explains why we found only trace amounts of CHEB at the lowest weight time in the HDS of THDBT and HHDBT in the absence of H_2S and MPi. In the presence of 1 kPa MPi, the hydrogenation of CHEB was strongly inhibited. Its conversion was only 33% at the lowest weight time and reached 95% at $\tau = 3.5$ g min/mol. This explains why CHEB was present only in the presence of a substantial amount of MPi.

4. Discussion

4.1. Hydrodesulfurization

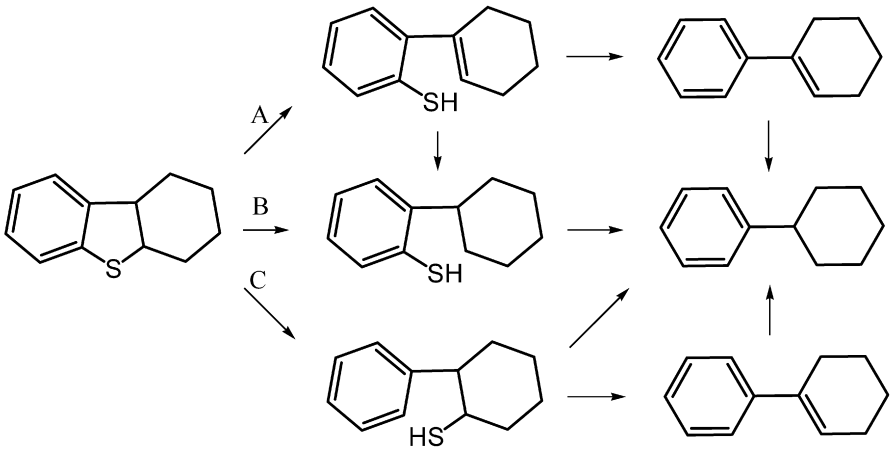
In principle, the breaking of a C–S bond over metal-sulfide catalysts may occur by elimination to form H_2S and an alkene or by hydrogenolysis to form H_2S and an alkane [20]. The more common anti-elimination involves breaking of the α-carbon-S bond and the β-carbon-H bond in the *trans* position, leading to the formation of a double bond. Syn elimination, although less favorable, is possible as well [11,12]. In the hydrogenolysis reaction, a C–S bond is broken, and C–H and S–H bonds form simultaneously. For aliphatic thiols, both elimination and hydrogenolysis are known to occur, as demonstrated by experimental [21] and theoretical [22] studies of the HDS of ethanethiol to ethene and ethane over metal sulfide catalysts.

Arylthiols also undergo a reaction that appears to be a direct C–S bond breaking. For instance, the direct desulfurization products of thiophenol and (DM)DBT are mainly benzene and (DM)BP, respectively [7–9,23], as confirmed by the results of the HDS of thiophenol and DBT in the present study. In all the HDS reactions of DBT that we performed, BP was a primary product and the sole product of the DDS pathway (Fig. 1). Thiophenol reacted very rapidly and was converted completely to benzene under our conditions. The HDS mechanism may consist of an actual hydrogenolysis reaction, in which thiophenol or DBT and hydrogen atoms on the catalyst surface react directly to benzene or BP, respectively. In the case of DBT, the reaction must be a two-step process to break two aryl C–S bonds (Scheme 2A), with an initial reaction to 2-phenyl-thiophenol followed by a reaction to BP [24]. The further reaction of the thiol intermediate must be very rapid, because this compound was never found in the HDS of DBT, and our results show that thiophenol reacted very rapidly under these conditions. Organometallic studies [25–30] have shown that a metal atom can be inserted into a C–S bond of benzothiophene and that the M–C bond can cleave to form a thiolate. However, it is doubtful that sufficient space is available around the less exposed metal atoms at the surface of a metal sulfide to allow such a reaction.

The hydrogenated intermediate THDBT underwent desulfurization under our conditions. The desulfurization product, CHB or CHEB, always behaved as a primary product in the HDS of THDBT in all of the reactions studied (Figs. 2–5). In reactions in the absence of MPi (Figs. 2–4 and 5B), CHB was the only primary desulfurized product found. In the presence of MPi (Figs. 4, 5C and 5D), CHEB behaved as a primary product as well. Its selectivity decreased with weight time, indicating that it reacted further. CHB behaved as a secondary product in the presence of MPi but the absence of H_2S and as a (quasi-) primary product in the presence of MPi as well as H_2S. The selectivities and yields of CHB increased with weight time, and CHB was the final product of the desulfurization of THDBT. The hydrogenation of CHEB to CHB in the presence of THDBT was very fast under our conditions and was strongly inhibited by MPi (Fig. 10), indicating that the desulfurization of THDBT to CHB proceeded by the CHEB intermediate. CHEB was seen as a primary product only when MPi was present to inhibit the rapid hydrogenation of CHEB to CHB. In contrast, in the presence of both MPi and H_2S, H_2S decreased the yield of CHEB; thus, the hydrogenation of CHEB to CHB was relatively fast, and both CHB and CHEB behaved as primary products.

The reaction of THDBT to CHEB may occur through hydrogenolysis of the two C–S bonds (Scheme 3). The C(5a)–S bond is an aryl C–S bond and the C(4a)–S bond is a vinyl C–S bond (Scheme 2B). Direct elimination of H_2S from THDBT cannot occur. A double-bond shift would allow elimination to occur [17]; for instance, 2,3,4,4a-THDBT could be formed from 1,2,3,4-THDBT and undergo elimination to 2-phenyl-1,3-cyclohexadiene. This diene would be partially hydrogenated to cyclohexen-2-yl-benzene and cyclohexen-1-yl-benzene (CHEB), but because we did not observe cyclohexen-2-yl-benzene, we assume that this double bond shift and elimination mechanism did not play an important role. Our experimental results do not provide an unequivocal answer to the question of which C–S bond breaks first. Both possibilities (Scheme 3) give the same hydrocarbon intermediate CHEB. The vinylic and arylic C–S bonds can be broken in a homogeneous solution of organometallic complexes of benzothiophene [29,30].

When HHDBT was used as a reactant, the desulfurization product, CHB or CHEB, behaved as a primary product in most reactions (Figs. 7–9). In the HDS of HHDBT at 300 °C and 0 kPa H_2S or at 340 °C and 35 kPa H_2S, the selectivity of CHB decreased significantly with decreasing weight time, suggesting that CHB was a secondary product. This may be due to the rapid conversion of HHDBT to THDBT and the formation of CHB from THDBT; however, the possibility that CHB is a primary product, formed at a low rate, cannot be excluded. In the HDS of HHDBT at 300 °C in the presence of MPi, CHEB also was found and behaved as a primary product; however, its selectivity was always low and it was never the sole primary product. Even in the presence of 1.5 kPa MPi and 0 kPa H_2S, the further reaction of THDBT was very slow, the decrease in the selectivity of CHEB and increase in the selectivity of CHB were slow, and both CHEB and CHB behaved as primary products (Fig. 8B). The HDS of THDBT demonstrated that when the HDS reaction proceeded by CHEB to CHB, CHEB could behave as the sole primary product and CHB could behave as a secondary product. This indicates that, unlike the desulfurization of THDBT, the desulfurization of HHDBT led to the simultaneous formation of CHEB and CHB, and CHEB reacted further to CHB.



Scheme 4. Possible reaction pathways in the desulfurization of HHDBT.

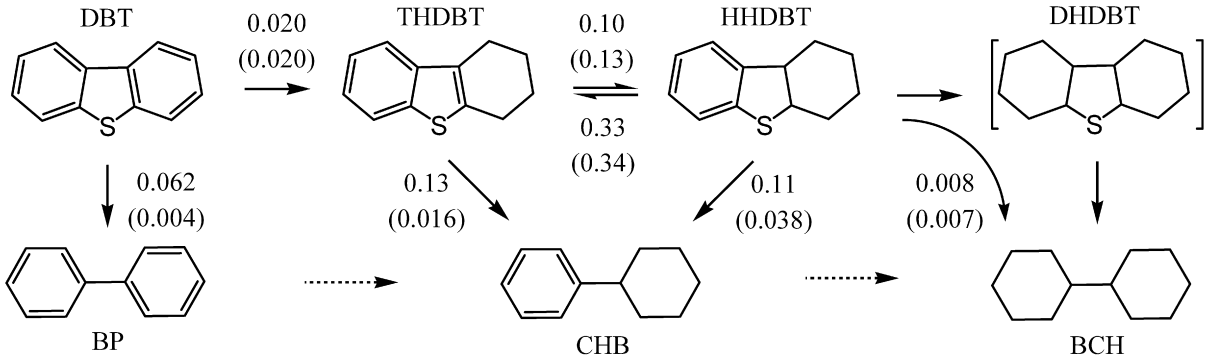
The formation of CHB and CHEB indicates that both hydrogenolysis and elimination reactions occurred in the desulfurization of HHDBT. The two C–S bonds of HHDBT are an aryl C–S bond [C(5a)–S, Scheme 2C] and a cycloalkyl C–S bond [C(4a)–S, Scheme 2C]. Scheme 4 shows three possible reaction pathways in the desulfurization of HHDBT. If the cycloalkyl C–S bond is broken first, then HHDBT can convert to 2-cyclohexyl-thiophenol by hydrogenolysis (pathway B) and to 2-cyclohexen-1-yl-thiophenol by elimination (pathway A). Elimination must proceed by the less likely syn elimination, and thus the cycloalkyl C–S bond is more likely to be broken by hydrogenolysis. If the aryl C–S bond is broken first, it can be broken only by hydrogenolysis, after which 2-phenyl-cyclohexanethiol forms (pathway C). A calculation of the desulfurization of dihydrobenzothiophene over a Mo_3S_9 cluster by Yao et al. [31] showed that hydrogenolysis of the aryl C–S bond is favored over that of the alkyl C–S bond in dihydrobenzothiophene. If this conclusion were to also hold for HHDBT, then pathway C would be favored over pathways A and B. Cleavage of the cycloalkyl C–S bond in the formed 2-phenyl-cyclohexanethiol can occur by elimination to CHEB and by hydrogenolysis to CHB. The ratio of CHEB to CHB in the HDS of HHDBT at 300 °C and 35 kPa H_2S in the presence of 1 kPa MPi was 0.5 at the lowest weight time and 0.15 at the highest weight time, much lower (about sixfold) than the cyclohexene/cyclohexane ratio in the HDS of cyclohexanethiol under the same conditions. Due to stronger adsorption, the hydrogenation of CHEB to CHB is probably much faster than that of cyclohexene to cyclohexane.

Because we did not observe DHDBT in the HDS of DBT, THDBT, and HHDBT, we did not study its HDS. A minor amount of BCH formed in the HDS of DBT, THDBT, and HHDBT at 300 °C, whereas it was a major product (and behaved as a secondary product) in the HDS of THDBT and HHDBT at 340 °C in the absence of H_2S or MPi. In some reactions, a trace amount of 1-cyclohexyl-cyclohexene was found at low weight time. The hydrogenation of CHEB (Section 3.5) demonstrated no further hydrogenation of CHB to BCH. Based on these findings, we believe that BCH is formed by hydrogenation of HHDBT to DHDBT, which then quickly converts to BCH. Both C–S bonds of DHDBT are cycloalkyl C–S bonds. The mechanism of the initial cycloalkyl C–S bond-breaking in DHDBT is unclear; both hydrogenolysis and elimination are possibilities. As proposed by Li et al. [17], a cycloalkylthiol (or cycloalkylthiolate) rather than a cycloalkenylthiol (or cycloalkenylthiolate) is predominantely formed. On the other hand, as shown by cyclohexanethiol, a cycloalkylthiol (or cycloalkylthiolate) can undergo elimination, which would explain why we found 1-cyclohexyl-cyclohexene at low weight time. This would mean that in the HDS of DHDBT, the initial C–S bond-breaking occurs inside a ring by hydrogenolysis, whereas the second C–S bond-breaking of the acyclic cyclohexanethiol occurs through both elimination and hydrogenolysis.

4.2. Reaction rate

The HDS reactions of DBT, THDBT, and HHDBT with different initial partial pressures showed that at 300 °C and 35 kPa H_2S, the reaction of DBT and THDBT was between first and zero order and that of HHDBT was first order. The different kinetic orders of DBT, THDBT, and HHDBT must be due to the different adsorption constants. As shown in Scheme 2, the DBT molecule is flat and is the most aromatic of the three molecules, due to conjugation of the two phenyl rings and the sulfur atom. Due to the 4a–9b double bond, the THDBT molecule is nearly flat, and the double-bond conjugation with the phenyl ring and the sulfur atom makes it more strongly aromatic than the HHDBT molecule, which is not flat and contains only a conjugation of the phenyl ring with the sulfur atom. As a result, the adsorption of DBT and THDBT is stronger than that of HHDBT, and these molecules have different kinetic orders. The rate constants of the reactions in the network of the HDS of DBT over Mo/γ-Al_2O_3 at 300 °C and 0 and 35 kPa H_2S were calculated by fitting the experimental data at conversion $<$20% and by assuming zero-order kinetics for DBT and THDBT and first-order kinetics for HHDBT. The influence of the H_2 and H_2S pressure were included in the kinetic constants. Nevertheless, the rate constants obtained by assuming first-order and zero-order kinetics were almost the same, because we used the experimental data at low conversion, and thus the partial pressure of the reactant hardly changed.

The kinetic results at 300 °C and 0 kPa H_2S (Table 1 and Scheme 5) show that the reaction of HHDBT to BCH was the slowest step in the network. This must be due to the slow hydrogenation of HHDBT to DHDBT, because the desulfurization of DH-DMDBT is very fast [17], and DHDBT was not observed in our experiments. Therefore, we assume that the rate of the reaction of HHDBT to BCH was the same as that of the hydrogenation of HHDBT to DHDBT. The second-slowest step, the hydrogenation of DBT to THDBT, was about threefold faster than the hydrogenation of HHDBT to DHDBT, proving that the hydrogenation was more difficult for the second phenyl ring than for the first phenyl ring. This is a well-known phenomenon in the hydrogenation of polycyclic aromatics. Both the hydrogenation of THDBT to HHDBT and the dehydrogenation of HHDBT to THDBT are very fast, the latter being the fastest. These data, along with the reaction profiles of the HDS of THDBT and HHDBT (Figs. 2 and 6), suggest that these two molecules tended to equilibrium. The THDBT/HHDBT ratios at the highest weight time were 4.3 in the reaction of THDBT and 3.5



Scheme 5. Rate constants (in kPa mol/(g min) for the HDS of DBT and HHDBT and in mol/(g min) for HDS of HHDBT) in the reaction network of the HDS of DBT over Mo/γ-Al_2O_3 at 300 °C and 5.0 MPa in the absence and presence (in parentheses) of 35 kPa H_2S.

Table 1
The rate constants (see Scheme 1) in kPa mol/(g min) for DBT and HHDBT and in mol/(g min) for HHDBT for the HDS of DBT, THDBT, and HHDBT over Mo/γ-Al_2O_3 at 300 °C and 5.0 MPa

Reactant	P_{H_2S} (init) (kPa)	P_{MPi} (init) (kPa)	Rate constant		
			k_{HYD}	k_{DDS}	
DBT	0	0	0.020 ± 0.003	0.062 ± 0.003	
	35	0	0.020 ± 0.001	0.004 ± 0.001	
	0	1	0.005 ± 0.001	0.028 ± 0.001	
	35	1	0.004 ± 0.002	0.002 ± 0.001	
			k_{TH}	k_{TC}	
THDBT	0	0	0.10 ± 0.02	0.13 ± 0.02	
	35	0	0.13 ± 0.02	0.016 ± 0.01	
	0	1	0.018 ± 0.003	0.033 ± 0.001	
	35	1	0.025 ± 0.002	0.004 ± 0.001	
			k_{HT}	k_{HC}	k_{HB}
HHDBT	0	0	0.33 ± 0.02	0.11 ± 0.01	0.008 ± 0.009
	35	0	0.34 ± 0.02	0.038 ± 0.01	0.007 ± 0.005
	0	1	0.038 ± 0.008	0.014 ± 0.002	
	35	1	0.035 ± 0.011	0.005 ± 0.002	

in the reaction of HHDBT. The rate of the DDS of DBT was about 2.5-fold higher than the rate of HYD of DBT, in agreement with the higher selectivity for DDS in the HDS of DBT. As expected, the desulfurization reactions of THDBT and HHDBT also were fast, about 2.5-fold faster and twofold faster, respectively, than the DDS of DBT.

Table 1 and Scheme 5 characterize the effect of H_2S on the kinetic results of the HDS of DBT and its intermediates at 300 °C. In the presence of 35 kPa H_2S, the rate constants of the desulfurization reactions decreased, whereas those of the (de)hydrogenation reactions hardly changed. Consequently, the slowest step in the reaction network became the DDS of DBT to BP. The hydrogenation of HHDBT and DBT were the next-slowest steps. The desulfurization of THDBT and HHDBT also slowed down in the presence of H_2S. In that case, the desulfurization of HHDBT was slightly faster than that of THDBT due to the stronger inhibition of THDBT by H_2S. The interconversion of THDBT and HHDBT remained the fastest reaction in the network. This and the reaction profiles (Figs. 3 and 7) suggest that these two molecules tended to equilibrium. The THDBT/HHDBT ratios at the highest weight time were 2.4 in the reaction of THDBT and 1.9 in the reaction of HHDBT. The THDBT/HHDBT ratio at the highest weight time at 35 kPa H_2S (∼2.4) was lower than that at 0 kPa H_2S (∼3.5), possibly due to the influence of the fast desulfurization of THDBT and HHDBT at 0 kPa H_2S on the observed THDBT/HHDBT ratio.

The rate constant of the hydrogenation of DBT at 35 kPa H_2S over Mo/γ-Al_2O_3 was 1.7-fold slower than that of DMDBT, and the interconversion of THDBT and HHDBT was much slower than that of TH-DMDBT and HH-DMDBT [17], due to the electron-donating effect of the methyl groups of DMDBT and its intermediates. The methyl groups of DMDBT retarded its desulfurization by steric hindrance; as a result, the rate constant of desulfurization of DBT was about fourfold greater than that of DMDBT. The rate constants for the desulfurization of HHDBT and HH-DMDBT were equal within the uncertainty of the measurement. The desulfurization of THDBT was about sixfold slower than that of TH-DMDBT, possibly due to the effect of electron donation by the methyl group.

4.3. Effects of H_2S and MPi on the HDS of DBT, THDBT, and HHDBT

It is well known that H_2S strongly inhibits the DDS pathway of the HDS of DBT but only slightly inhibits the HYD pathway [3,12,15,32,33]. Our results show that the rate constant of the DDS pathway of the HDS of DBT at 35 kPa H_2S was about 15-fold lower than that at 0 kPa H_2S, whereas the rate constant of the HYD pathway hardly changed. As shown in Figs. 2, 3, 6, and 7 and Table 1, H_2S also strongly inhibited the desulfurization of THDBT and HHDBT but hardly affected their hydrogenation and dehydrogenation. The rate constants of the desulfurization of THDBT and HHDBT at 35 kPa H_2S were about eightfold lower and threefold lower, respectively, than those at 0 kPa H_2S. The degree of inhibition of the desulfurization of DBT, THDBT, and HHDBT by H_2S was in the order DBT (15) > THDBT (8) > HHDBT (3). A similar degree of inhibition by H_2S was observed in the presence of MPi (Table 1). Molecular modeling calculations showed that the hydrogenation of the neighboring phenyl ring increased the electron density on the sulfur atom and thus increased the interaction with the active sites of the catalyst [34]. Therefore, the strength of the M–S bond of σ-adsorption should be in the order HHDBT > THDBT > DBT, and, due to the competition between these molecules and H_2S for the active site, the degree of inhibition of H_2S should be in the reverse order.

Our results confirm that nitrogen-containing molecules are strong poisons in the HDS of DBT and DMDBT, especially in the HYD pathway [15,35–37]. The conversion of DBT in the presence of 1 kPa MPi was about half that in the absence of MPi at 300 °C at 0 kPa H_2S, whereas the selectivity of BP increased. Table 1 gives the rate constants for the HDS of DBT, THDBT, and HHDBT over Mo/γ-Al_2O_3 at 300 °C and 5.0 MPa in the presence of 1 kPa MPi. The rate constants of the HYD and DDS pathways of the HDS of DBT were about fourfold lower and twofold lower, respectively, in the presence of than in the absence of MPi at 0 and 35 kPa H_2S. This indicates that MPi inhibited both pathways, the HYD pathway to a greater extent than the DDS pathway.

MPi also strongly suppressed the HDS of THDBT and HHDBT. The conversion of THDBT at 300 °C in the presence of 1 kPa MPi was almost fourfold lower than that at 0 kPa MPi, and the selectivity of HHDBT at zero weight time decreased (cf. Figs. 2 and 4).

A similar result was observed at 340 °C (Fig. 5). The rate constant of the hydrogenation of THDBT was about fivefold lower in the presence of than in the absence of 1 kPa MPi at 300 °C and 0 or 35 kPa H_2S, whereas the rate constant of its desulfurization was about fourfold lower (Table 1). The conversion of HHDBT at 300 °C, 0 kPa H_2S, and 1 kPa MPi was almost sevenfold lower than that at 0 kPa MPi, and the selectivity of THDBT at zero weight time also decreased (Figs. 6 and 8). A similar decrease was observed at 340 °C (Fig. 9). The rate constant of the dehydrogenation of HHDBT was about ninefold lower in the presence of than in the absence of 1 kPa MPi at 300 °C and 0 or 35 kPa H_2S, whereas the rate constant of its desulfurization was about eightfold lower. All of these findings indicate that the HDS of THDBT and the HDS of HHDBT were strongly inhibited by MPi, (de)hydrogenation to a greater extent than desulfurization. This proves that the nitrogen-containing compound adsorbed more strongly than DBT and its partially hydrogenated intermediates on the catalytic sites and adsorbed on both the desulfurization and (de)hydrogenation sites.

The degree of inhibition of MPi on the desulfurization of DBT, THDBT, and HHDBT differed in the following order: HHDBT > THDBT > DBT. This must be due to the differing strengths of adsorption of these molecules on the catalytic sites compared with MPi. The order of their aromaticity, and thus their π adsorption constants, is DBT > THDBT > HHDBT. Therefore, the degree of inhibition of MPi on (de)hydrogenation of those molecules was in the reverse order. The order of the degree of inhibition of MPi on the desulfurization of these molecules was opposite that of the inhibition of H_2S. We cannot explain this finding based on our present findings.

We also studied the HDS of DBT, THDBT, and HHDBT in the absence and presence of H_2S and MPi at 340 °C. The reactions of these three molecules were greatly enhanced at higher reaction temperatures, with desulfurization more strongly promoted than (de)hydrogenation, as also was observed for DBT and DMDBT on sulfided Ni–Mo and Co–Mo catalysts and on Pd catalysts [16,32–38], because desulfurization has a higher activation energy than (de)hydrogenation.

5. Conclusion

A detailed study of the HDS reaction network of DBT over Mo/γ-Al_2O_3 was carried out at 300–340 °C and 5 MPa in the presence and absence of H_2S and MPi. Two intermediates of DBT—tetrahydro-DBT and hexahydro-DBT—were synthesized, and their HDS was investigated. The reactions of some desulfurization intermediates also were studied. From the resulting data, the rate constants of all of the steps in the kinetic network of the HDS of DBT were obtained.

The HDS of DBT occurred mainly through the DDS pathway in the absence of H_2S and through the HYD pathway in the presence of H_2S. The hydrogenation of THDBT and dehydrogenation of HHDBT was fast, and these molecules tended to equilibrium at high weight time. CHEB was observed as a desulfurization intermediate in the HDS of THDBT and HHDBT, indicating that THDBT underwent desulfurization by hydrogenolysis to CHEB, followed by hydrogenation of CHEB to CHB. HHDBT underwent desulfurization by cleavage of the aryl C–S bond by hydrogenolysis, followed by cleavage of the cycloalkyl C–S bond in the formed 2-phenylcyclohexanethiol by elimination to CHEB and by hydrogenolysis to CHB. Among the three sulfur-containing molecules, the desulfurization of THDBT was fastest in the absence of H_2S, and that of HHDBT was fastest in the presence of H_2S.

H_2S strongly inhibited the desulfurization of DBT, THDBT, and HHDBT in the order DBT > THDBT > HHDBT, but hardly affected their (de)hydrogenation. MPi also strongly inhibited the HDS of these molecules, (de)hydrogenation more than desulfurization. The order of inhibition by MPi was HHDBT > THDBT > DBT. The differing degrees of inhibition were due to the different strengths of adsorption of these molecules on the catalytic sites.

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