Hydrodesulfurization of Alkyldibenzothiophenes over a NiMo/Al₂O₃ Catalyst: Kinetics and Mechanism

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The transformation mechanism of dibenzothiophene, 4-methyldibenzothiophene, 4,6-dimethyldibenzothiophene, and 2,8-dimethyldibenzothiophene has been studied in a batch reactor over an industrial NiMo/Al₂O₃ hydrotreating catalyst at 573 K under 5 MPa of hydrogen pressure. A detailed mechanistic study including competitive catalytic experiments proved that the adsorption of the most refractory molecules at the catalyst surface was not the rate-determining step for their transformation. Our results imply that the hydrodesulfurization of these compounds occurs on one single type of sites by a flat adsorption, leading to a preliminary partial hydrogenation of one aromatic ring. Variations in reactivities of the dibenzothiophene derivatives were thus explained by different reaction rates for the C-S bond scission due to steric hindrance generated by the methyl substitution near the sulfur atom. © 1997 Academic Press

INTRODUCTION

Recent and future legislation in European countries concerning air pollution by diesel exhaust gas prompts refiners to reduce considerably the sulfur content of gas oil, from 0.2 wt% in 1994 to 0.05 wt% in 1996 and probably lower in the near future. For the sulfur compounds, the high conversions thus required can be achieved with the present hydrodesulfurization processes only by using expensive and drastic methods such as increasing the temperature and the pressure in the reactor or lowering the liquid hourly space velocity. Development of new catalysts is therefore a challenge for refiners and catalyst producers, but such a success could be more easily achieved by a better knowledge of the deep hydrodesulfurization process. Many researches have been performed in the past 20 years to find out which compounds are refractory to the HDS process (1). These molecules are now known to be alkyldibenzothiophenes, and especially compounds substituted in the 4 and/or 6 positions (2). Many authors have proposed hypotheses to explain the lower reactivity of these compounds compared to the unsubstituted dibenzothiophene. The discussions are mainly based on two proposals: the most generally accepted one considers that the sulfur compounds have different adsorption constants according to their structure. The low reactivity of the alkyldibenzothiophenes could thus be due to their lower adsorption constant at the catalyst surface. A second hypothesis suggests on the contrary that the different reactivities result from different surface reaction rates. An unequivocal explanation for these different reactivities is however difficult to be found by reading conscientiously the corresponding literature. The researches run in this field by the scientists have been conducted under different experimental conditions according to their speciality, leading however often to ambiguous and even contradictory results.

To illustrate the main results, we first report the work of Houalla *et al.* published in 1980 (3), dealing with the transformation of dibenzothiophene (DBT), 2,8-dimethyldibenzothiophene (2,8-DMDBT), 3,7-dimethyldibenzothiophene (3,7-DMDBT), and 4,6-dimethyldibenzothiophene (4,6-DMDBT). The authors noticed a decreasing reactivity in the order DBT, 2,8-DMDBT, 3,7-DMDBT, 4,6-DMDBT; this phenomenon was attributed to different adsorption strengths of the studied molecules on the catalyst surface. Ma *et al.* (4) observed the same inhibition by the neighboring methyl groups on the sulfur atom and proposed similarly a possible steric hindrance of the methyl groups limiting the adsorption of the molecules on the catalyst.

The second hypothesis is illustrated by the study of Kabe *et al.* (5). They have also compared the reactivities of different mono- and polyalkyldibenzothiophenes: 4-MDBT and 4,6-DMDBT were found to be the only ones to have a very low reactivity compared to that of DBT. This was explained by a steric hindrance generated by the methyl groups of the adsorbed molecule to proceed to the C–S bond scission. Unlike previously published results, they found more important values for the adsorption equilibrium constants in the cases of 4-MDBT and 4,6-DMDBT than in the case of DBT.

The evident confusion and lack of information concerning the understanding of the low reactivities of 4-methyland 4,6-dimethyldibenzothiophene are also probably related to a poor knowledge of the catalytic sites (nature, number...) involved in their transformation.

Two modes of adsorption can be taken into account: a flat adsorption by the π -electrons of the aromatic system or a bonding via the sulfur atom of the molecule. It is generally reported that the π -adsorption favors hydrogenation reactions, whereas the sulfur adsorption is related to desulfurization reactions. Several authors (6–8) claimed that these two different kinds of adsorption modes are required for the hydrodesulfurization of the studied molecules and connected the low reactivity of 4,6-DMDBT to a difficult adsorption by the sulfur atom on account of the steric hindrance.

However, the possibility of two different adsorption modes for the transformation of DBT and its derivatives has not yet been actually proven. Considering that sulfur adsorption was improbable, Singhal (9) has proposed a mechanism involving a preliminary hydrogenation of the molecule thus occuring after a π -adsorption, leading to a dihydrodibenzothiophene, a common species to the both routes of transformation usually observed. A study by Zdrazil about the transformation of thiophene, benzothiophene, and dibenzothiophene supports this hypothesis of such hydrogenated intermediates (10).

Considering that the various explanations for the mechanism of DBT transformation are quite contradictory, the aim of the present study is to reexamine the transformation of the refractory alkyldibenzothiophenes in order to precise their reaction scheme and to explain the lower reactivity of 4,6-DMDBT.

For this purpose, we have synthesized the required molecules and compared their reactivities in a batch reactor, on an industrial NiMo/Al₂O₃ hydrotreating catalyst, in separate and competitive experiments.

EXPERIMENTAL PROCEDURE

Materials

Dibenzothiophene (98% purity) was obtained from Sigma–Aldrich–Fluka and used without further purification. 4-Methyldibenzothiophene (93% purity) was synthesized according to the method of Gerdil *et al.* after optimization, by metallation and subsequent methylation of DBT (11). 4,6-Dimethyldibenzothiophene (>99% purity) was prepared by a four-step method (25% global yield) starting from a coupling reaction of *ortho*-thiocresol and 2-bromo-3-nitrotoluene as previously described (12). 2,8-Dimethyldibenzothiophene (>99% purity) was synthesized in two steps with 30% global yield (Fig. 1). The first step, described by Neumoyer (13), consists in a bromination of DBT in refluxing acetic acid for 4 h. 2,8-Dibromodibenzothiophene is separated from monobromodibenzothiophene by recrystallization in acetic anhy-



FIG. 1. Synthesis of 2,8-dimethyldibenzothiophene.

dride and methylated by methyl magnesium iodide in ether. This last step is catalyzed by a nickel II complex (Kumada type reaction).

For the alkyldibenzothiophenes hydrodesulfurization, the catalyst used was an industrial NiMo/Al₂O₃ (Mo, 9 wt%; Ni, 2.4 wt%). This catalyst was provided as extrudates (bulk density, 0.71 g cm⁻³; pore volume, 0.48 cm³ g⁻¹; surface area, 185 m² g⁻¹). The extrudates were crushed, screened (80–120 μ m), and then sulfided *ex situ* by a H₂–H₂S (15%) flow at 673 K for 4 h before use.

Reactor and Analytical

Studies were performed in a 200-cm³ stirred slurry tank reactor operating in batch mode. The autoclave is equipped with a hollow-shaft six-bladed magnetically driven turbine with four baffles on the wall to prevent vortex formation. The samples are collected through a 1/16 in. diameter tube; hydrogen is introduced through a pressure controller which maintains a constant pressure during the course of the experiment.

In each run, the autoclave was charged with 0.1 to 0.5 g of reactant dissolved in 80 ml dodecane, after having checked that the reaction order toward the sulfur compound was zero. Freshly sulfided catalyst (0.1 to 1 g) was added to the solution. The reactor was flushed with nitrogen and heated to reach the reaction temperature of 573 K; nitrogen was then replaced by hydrogen and the stirring was started, indicating the zero of the reaction time. Sample were periodically removed during the reaction course and analyzed by gas chromatography. When the influence of H₂S on the convertion was studied, 0.35 g of dimethyldisulfide (DMDS) was added to the solution containing in this case 1.3 mmol of substrate. DMDS is rapidly hydrogenolyzed in H₂S in our operating conditions providing a molar ratio H₂S/DBT then equal to 6, a value which is closed to the conditions existing in a refinery process when an almost complete desulfurization of a gas oil feed is achieved.

GC analyses were performed using an apolar column (HP 5, 5% phenylmethylsilicone, 30 m \times 0.53 mm) equipped with a FID detector. The column temperature was programmed between 368 and 573 K. The different intermediates and products of the reaction were identified by GC/MS analyses.

Control of the Kinetic Regime

A set of experiments was performed to check the absence of intraparticle and interphase mass transfer limitations. Different weights of catalyst were tested (0.1 to 1 g) and the results indicated that the kinetic regime was established in all cases. The effect of the stirring rate and the granulometry of the catalyst has been controlled (14). It appeared that no diffusional problem could occur under our operating conditions when the mass of the catalyst was limited to 1 g and the stirring rate was fixed to at least 1500 revolutions per minute.

Kinetic Calculations

Some experiments were realized on single products and others on equimolar mixtures of two compounds thus reacting in competition.

Hydrodesulfurization of a single compound. A typical reaction course according to the time is pointed out in Fig. 2. The initial rate of the DBT transformation can be obtained by the slope to the DBT curve at the origin.

The yields of the different products can also be plotted versus the conversion, in order to determine the reaction scheme and the product selectivities, as will be illustrated later in Figs. 4 and 5.

Hydrodesulfurization in competitive experiments. In competitive experiments, two compounds *A* and *B* are considered to compete for adsorption on the same sites. *R* is the common reactant to the transformation of *A* and *B*.

$$R \xrightarrow{k_{1A}} \underline{R}$$

$$A \xrightarrow{k_{1A}} \underline{A} \quad \underline{A} + \underline{R} \xrightarrow{k_{A}} C$$

$$B \xrightarrow{k_{1B}} B \quad \underline{B} + \underline{R} \xrightarrow{k_{B}} D,$$

where the components underlined (i.e., <u>A</u>) correspond to the adsorbed species, k_{1i} (respectively, k_{-1i}) represents the rate constant of adsorption (respectively, desorption) of component *i* and k_i the rate constant of the surface reaction of component *i*.

At the stationary state of <u>A</u>

$$k_{1A} \cdot [A] \cdot [S] = k_{-1A} \cdot [\underline{A}] + k_A \cdot [\underline{A}] \cdot [\underline{R}], \qquad [1]$$



FIG. 2. Transformation of a single molecule (DBT): conversion versus time. Experimental conditions: 563 K, 50 MPa, NiMo catalyst. (+, DBT; \bullet , BP; ×, CHB; \triangle , HN.)

then the formation rate of *C* is

$$v_C = k_A \cdot [\underline{A}] \cdot [\underline{R}], \qquad [2]$$

where [A] can be expressed by

$$[\underline{A}] = \frac{k_{1A} \cdot [A] \cdot [S]}{k_{-1A} + k_A \cdot [\underline{R}]}.$$
[3]

In this expression, [i] represents the concentration of component *i* after a known reaction time, [S] is the concentration of active sites at the surface, and $[\underline{R}]$ is the concentration of the hydrogen adsorbed on the catalyst surface.

Similarly, at the stationary state of $[\underline{B}]$

$$k_{1B} \cdot [B] \cdot [S] = k_{-1B} \cdot [\underline{B}] + k_B \cdot [\underline{B}] \cdot [\underline{R}], \qquad [4]$$

then the formation rate of D is

$$v_D = k_B \cdot [\underline{B}] \cdot [\underline{R}], \qquad [5]$$

where [*B*] can be expressed by

$$[\underline{B}] = \frac{k_{1B} \cdot [\underline{B}] \cdot [\underline{S}]}{k_{-1B} + k_B \cdot [\underline{R}]}.$$
[6]

[<u>*R*</u>] is supposed to be the same in both expressions; the rate ratio is then expressed by

$$\frac{v_D}{v_C} = \frac{k_B \cdot k_{1B} \cdot [B]}{k_A \cdot k_{1A} \cdot [A]} \cdot \frac{k_{-1A} + k_A \cdot [\underline{R}]}{k_{-1B} + k_B \cdot [\underline{R}]} = \frac{d[B]}{d[A]}.$$
 [7]

From integration of this equation, the reactivity ratio $R_{B/A}$ between the considered molecules *A* and *B* can be obtained (15–17).

$$\frac{\log \frac{|\mathbf{B}|}{|\mathbf{B}_0|}}{\log \frac{|\mathbf{A}|}{|\mathbf{A}_0|}} = \frac{k_B \cdot k_{1B}}{k_A \cdot k_{1A}} \left(\frac{k_{-1A} + k_A[\underline{R}]}{k_{-1B} + k_B[\underline{R}]} \right) = R_{B/A}.$$
 [8]

The ratio R is, at constant temperature, independent of the mixture composition and extent of conversion. At relatively low hydrogen pressure, the surface reaction is the rate-determining step and R can be expressed as a function of adsorption equilibrium constants and rate constants

$$R_{B/A} = \frac{k_B K_B}{k_A K_A}$$
[9]

with

$$K_i = \frac{k_{1i}}{k_{-1i}} \tag{10}$$

representing the adsorption equilibrium constant of compound *i* at the surface.

It has been checked (14) that under our experimental conditions, a pressure of 5 MPa still corresponds to the range of low hydrogen pressure and thus that the above expression can be used. Therefore, a comparison of the R

values with the rate ratios k_B/k_A calculated for the transformation of each product in separate experiments allows the determination of the adsorption equilibrium constants ratios K_B/K_A .

RESULTS

Transformation of the Single Molecules

The transformation study of the different compounds indicates a reaction scheme in agreement with the proposals of the literature (18, 19). As schematized in Fig. 3, DBT and alkyl-DBT appear to be transformed according to two parallel routes. The first one, called the direct desulfurization pathway (DDS) first gives biphenyl derivatives (BP). These desulfurized molecules are then slowly hydrogenated into cyclohexylbenzenes (CHB). The second pathway, called the hydrogenation route (HYD) consists in a preliminary hydrogenation of one aromatic ring, giving tetrahydro- and hexahydrodibenzothiophene or analogues (HN). These intermediates can then be desulfurized to CHB.

The evolution of the reactant transformation is followed by regular samplings which are analyzed by gas chromatography. Product concentrations are determined and the selectivities are calculated. The curves representing the yield of products versus the conversion of the studied molecule, without or with H_2S present in the reactor, are given, respectively, in Figs. 4 and 5. The rates being drastically lowered by the presence of H_2S the conversion was in the latter case limited to 30%.

Considering first the case of DBT and 2,8-DMDBT transformations without H_2S , the major product observed is biphenyl (or dimethylbiphenyl), CHB appearing significantly only at conversions higher than 30% as a secondary



Cyclohexylbenzene (CHB)

FIG. 3. Transformation scheme of dibenzothiophene.

product. Hydrogenated products (HN) are only observed as traces. On the contrary, the products issued from the transformation of 4-MDBT and 4,6-DMDBT are mainly resulting from the hydrogenation pathway, leading to CHB and HN. Moreover, concerning the transformation of 4,6-DMDBT, the selectivity in BP remains very low, whatever the conversion.

The same tendency is observed when H_2S is present in the reactor: at comparable conversion, 4,6-DMDBT leads to the formation of less BP derivatives than DBT. It appears also that the selectivities for the products resulting from the hydrogenation route are increasing.

From the curves presented in Figs. 4 and 5, the selectivities in the different compounds can be evaluated. The values determined at 10% conversion are given in Tables 1 and 2.

The initial transformation rates of the different compounds were calculated from the slope to the reactant transformation curves similar to the one presented in Fig. 2. The quantification of the rates according to each pathway was performed using the initial transformation rates and the selectivities calculated at 10% conversion, taking into account that, at such a level of conversion, the hydrogenation of biphenyl into cyclohexylbenzene could be neglected (14).

The transformation rates of the studied molecules decreased in the order 2,8-DMDBT > DBT > 4-MDBT > 4,6-DMDBT whatever the operating conditions (Tables 1 and 2).

Without H_2S (Table 1), the 4,6-DMDBT was found to be about six times less reactive than the DBT and the 4-MDBT about three times less reactive. These results confirm that hydrodesulfurization of substituted DBT is inhibited by the presence of methyl groups at the carbon α to the sulfur atom. However, under the same conditions, the transformation of 2,8-DMDBT is more than two times faster than that of DBT, thus providing additional proof that the loss of reactivity in the case of 4,6-DMDBT was not due to the number of substituents but to their position. It must be pointed out that the calculation of rates according to each pathway clearly shows that the methyl-inhibition in the 4 and 6 positions only affects the DDS pathway, the hydrogenation rates being indeed similar for all the compounds.

When H₂S is present in the reactor (H₂S/DBT = 6), the global transformation rate is greatly lowered for all the compounds (Table 2), the order of reactivities remaining however similar. For example, the transformation rate of DBT under these conditions reaches only 7.5×10^{-8} mol s⁻¹ g⁻¹ instead of 180×10^{-8} mol s⁻¹ g⁻¹ without H₂S present in the reactor. This decrease in reactivity is similar concerning the transformation of 2,8-DMDBT (22×10^{-8} and 400×10^{-8} mol s⁻¹ g⁻¹) but is less important for the compounds methylated at positions close to the sulfur atom. By comparing the rates according to each pathway under both operating conditions, it is obvious that the desulfurization route is more



FIG. 4. Diagrams of yield versus conversion obtained for the transformation of DBT, 4-MDBT, 4,6-DMDBT, and 2,8-DMDBT without H₂S in the reactor. (\bullet , BP; *, CHB; \triangle , HN.)

inhibited by the presence of H_2S than the hydrogenation one.

Competitive studies were realized in order to understand if the decreasing reactivities of 4-MDBT and 4,6-DMDBT were due to a problem of adsorption on a catalytic site or to differences in the surface reaction rates.

Competitive Experiments

An equimolar mixture of two dibenzothiophene derivatives (noted A and B for simplification) in dodecane was introduced into the reactor and converted under the standard conditions without H₂S (NiMo catalyst, 50 MPa, 573 K). Samples were periodically removed at increasing conversion to allow the calculation of each reactant concentration (A and B). According to the competitive theory (see above), curves of $\ln(A/A_0)$ versus $\ln(B/B_0)$ are thus available. The straight lines obtained demonstrate the validity of the competitive experimental approach and allow the corresponding reactivity ratio *R* to be calculated (Fig. 6).

The rate constants ratio k_A/k_B is easily available through r_i values (initial transformation rate of compound *i*) since the considered reactants are present in equimolar proportions; this rates ratio, compared to the reactivity ratio obtained in competition, allowed the calculation of the adsorption equilibrium constants ratio K_A/K_B between the two considered molecules (see Table 3).

In all cases, the rate ratio k_A/k_B calculated from separate experiments is similar to the reactivity ratio *R* calculated

	Initial transformation rate (\times 10 ⁸ mol/(s · g))	<i>S</i> (BP) ^{<i>a</i>} (%)	S(CHB) ^a (%)	<i>S</i> (HN) ^{<i>a</i>} (%)	$\frac{\text{Desulfurization rate}}{(\times 10^8 \text{ mol}/(s \cdot g))}$	Hydrogenation rate (\times 10 ⁸ mol/(s · g))
DBT	180	87	6	7	157	23
4-MDBT	57	43	27	30	24	33
4,6-DMDBT	30	10	30	60	3	27
2,8-DMDBT	400	93	3	4	372	28

TABLE 1

Transformation of the Compounds without H₂S in the Reactor

^a Selectivities of each product calculated at 10% conversion.



FIG. 5. Diagrams of yield versus conversion obtained for the transformation of DBT, 4-MDBT, 4,6-DMDBT, and 2,8-DMDBT with H₂S present in the reactor. (\bullet , BP; *, CHB; \triangle , HN.)

from competitive experiments. Therefore, the adsorption equilibrium constants are almost the same for all the studied molecules, taking into account the limit of the precision during catalytic activity determination $(\pm 10\%)$.

DISCUSSION

It is difficult to compare our results (rate values) with those of the literature. The operating conditions (temperature, pressure, reactor...) are indeed very different from one group to another. Comparing only the classification for the reactivity of alkyldibenzothiophenes, it is clear that the transformation dibenzothiophene is inhibited by the presence of methyl groups near the sulfur atom, in accordance with all the published studies (3).

Moreover, the methyl substitution and the inhibiting effect of H_2S do not affect similarly the two parallel routes of transformation (DDS and HYD), the DDS one being principally inhibited (Tables 1 and 2). The inhibition by H_2S is particularly noticeable if we observe the DBT transformation which is essentially governed by this pathway. The global transformation of this compound is drastically lowered (24-fold) if H_2S is present in the reactor, though only a 7-fold decrease is observed in the case of 4,6-DMDBT.

Both methyl substitution and H₂S concentration significantly affect the direct desulfurization route. To afford deep

	Initial transformation rate (\times 10^8 mol/(s \cdot g))	S(BP) ^a (%)	S(CHB) ^a (%)	S(HN) ^a (%)	$\begin{array}{l} Desulfurization\ rate \\ (\ \times\ 10^8\ mol/(s \cdot g)) \end{array}$	$\begin{array}{l} Hydrogenation\ rate \\ (\ \times\ 10^8\ mol/(s\cdot g)) \end{array}$
DBT	7.5	70	20	10	5	2
4-MDBT	5.5	25	30	45	1.5	4
4,6-DMDBT	4.4	8	23	69	0.4	4
2,8-DMDBT	22	64	9	27	14	8

TABLE 2

Transformation of the Compounds with H₂S Present in the Reactor

^a Selectivities of each product calculated at 10% conversion.



FIG. 6. $\ln(A/A_0)$ versus $\ln(B/B_0)$ obtained in competitive experiments. (\heartsuit) *A*, DBT; *B*, 2,8-DMDBT. (\bigcirc) *A*, 4-MDBT; *B*, 4,6-DMDBT. (\times) *A*, DBT; *B*, 4-MDBT. (+) *A*, DBT; *B*, 4,6-DMDBT.

HDS, the hydrogenation route then appears to be of great importance for the conversion of alkyldibenzothiophenes and has to be developed (20, 21).

To understand which phenomenon could explain these inhibitions, and principally the effect of the methyl near the sulfur atom, a competitive study was performed. The results indicate that the adsorption equilibrium constants of all the dibenzothiophene derivatives are similar and that these compounds are identically adsorbed on the catalyst surface, probably via the π -electrons of the aromatic rings. Thus, the difference of reactivity observed between the alkyldibenzothiophenes cannot be explained by a different adsorption strength at the catalyst surface.

Taking into account these results, an adsorption by the sulfur atom is unrealistic. The constants of adsorption would be otherwise greatly different for molecules sterically hindered by methyl groups around the sulfur atom. Following this conclusion, we can then assume a flat adsorption of the DBT derivatives by the π -electrons of the aromatic system as proposed by Singhal *et al.* (9). This supposes a subsequent destabilization of the molecule, leading probably to a preliminary hydrogenation of at least one double bond.

If the adsorption strength is not responsible for the difference of reactivity observed between the various alkyldibenthiophenes, an explanation must be searched for in the mechanism of evolution of the adsorbed species.

The promotion of the desulfurization route in the case of the 2,8-disubstitution $(157 \times 10^{-8} \text{ mol s}^{-1} \text{ g}^{-1} \text{ for DBT}$

TABLE 3

Competitive Experiments (573 K, 50 MPa, No H₂S)

Two compounds A-B	Rates ratio k_A/k_B (single products)	Reactivity ratio $R_{A/B}$ (competitive experiments)	K_A/K_B
DBT-4-MDBT	3.2	4	1.3
4-MDBT-4,6-DMDBT	1.9	2.5	1.3
DBT-4,6-DMDBT	6	8	1.3
DBT-2,8-DMDBT	0.45	0.53	1.2



FIG. 7. Reaction scheme of DBT transformation involving a partially hydrogenated intermediate.

and 372×10^{-8} mol s $^{-1}$ g $^{-1}$ for 2,8-DMDBT without H₂S) clearly demonstrates that only the substitution near the sulfur atom inhibits the desulfurization route. To explain this rising activity, an analogy can be proposed with the hydrogenation of aromatics. Toluene is known to be more easily hydrogenated than benzene on sulfide catalysts (22) and we have also shown that on a NiMo catalyst, 3-methylbiphenyl was faster hydrogenated than biphenyl (14). In the case of 2,8-DMDBT, the transformation can then be exalted by an easier hydrogenation of an aromatic ring. The mechanistic scheme described by Singhal et al. (9) is in accordance with our observations. They proposed a common intermediate to the two routes of transformation, such as a dihydrodibenzothiophene. However, this very unstable species has never been detected in solution, it can probably only exist as an adsorbed intermediate. Markel and Angelici proposed a similar intermediate (dihydrothiophene) to explain the transformation of thiophene (23). The dihydrodibenzothiophene could then either be further hydrogenated into tetrahydro- and hexahydrodibenzothiophene or desulfurized by elimination to provide biphenyl. This last pathway has been proposed by Kasztelan to illustrate the HDS and HDN mechanisms (24). A possible structure for this adsorbed dihydrodibenzothiophene and its transformation according to the two pathways are presented in Fig. 7.

Therefore, the higher reactivity of 2,8-DMDBT is explained by an easier and faster formation of the partially hydrogenated intermediate. According to Houalla *et al.* (3), 2,8-DMDBT has almost the same reactivity as DBT. They use however for its transformation a CoMo catalyst that is known to be less hydrogenating than a NiMo one. We assume that in this case the poor hydrogenating properties of CoMo are not sufficient to exalt the transformation of 2,8-DMDBT compared to unsubstituted DBT.

For all the dibenzothiophene derivatives, the modifications in the global transformation rates with H_2S partial pressure could be explained by the competitive adsorption of the organic sulfur molecule and H_2S on the Mo coordinatively unsaturated sites. However, the DDS route was found to be more inhibited than the HYD one. This can be correlated to the mechanism proposed in Fig. 7, which requires the presence of a basic species. In such a mechanism, H_2 and H_2S are considered to be dissociatively adsorbed on the catalytic surface, over the coordinatively unsaturated molybdenum sites and over the sulfur ions according to

$$M^* + H_2 + \bullet S^{2-} \longrightarrow MH^- + \bullet SH^-$$
$$M^* + H_2S + \bullet S^{2-} \longrightarrow MSH^- + \bullet SH^-$$

In agreement with Kasztelan (24), we propose that the hydrogenation steps leading to partially hydrogenated DBT are a H^- or H^+ addition, whereas the desulfurization is the result of a basic attack by S^{2-} species. Therefore, the inhibiting effect of H_2S on the DDS route can be related to the lowering concentration of S^{2-} .

Moreover, for the transformation of 4-MDBT and 4,6-DMDBT, the inhibition of the only desulfurization pathway can be explained by a steric hindrance generated by the methyl groups for the basic attack.

CONCLUSION

We have followed the transformation of DBT, 4-MDBT, 4.6-DMDBT, and 2.8-DMDBT on a NiMo/Al₂O₃ catalyst in separate and competitive experiments. The obtained detailed kinetic study allows us to confirm the inhibiting effect both of methyl-substituents near the sulfur atom and of H₂S on the direct desulfurization route. We assume, according to the results of the competitive experiments, that all the studied molecules have similar adsorption equilibrium constants suggesting an unique flat mode of adsorption on the catalyst via the π -electrons of the aromatic system. The difference of reactivity must then be due to different reaction rates in the transformation of the adsorbed molecule. We thus propose that the HDS mechanism involves first a preliminary partial hydrogenation of the adsorbed aromatic system. On the same site, the considered intermediate, probably a dihydrodibenzothiophene, can then be further hydrogenated (following the known hydrogenation route) or desulfurized (DDS route) according to its structure: DBT or 2,8-DMDBT lead indeed preferentially to biphenyl derivatives whereas 4-MDBT and even more 4.6-DMDBT are transformed according to a hydrogenation pathway.

We have proven that the drastic decrease in the global transformation of substituted dibenzothiophenes, compared to dibenzothiophene itself, was principally due to a strong decrease in the direct desulfurization pathway, in relation with methyl steric hindrance. It is obvious that the hydrogenating properties of the catalyst involved in the HDS of refractory molecules are of great importance. We assume, that a more hydrogenating catalyst could allow an increasing global transformation rate through an increase of hydrogenation reactions. Experiments in this way are in progress.

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