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Hydrodesulfurization of Alkyldibenzothiophenes: Evidence of Highly Unreactive Aromatic Sulfur Compounds

M. Macaud,*,† A. Milenkovic,*,† E. Schulz,† M. Lemaire,† and M. Vrinat*,[1]

*Institut de Recherches sur la Catalyse, 2 Av. A. Einstein, 69626 Villeurbanne Cedex, France; and †Laboratoire de Catalyse et Synthèse Organique, IRC, UCBL, CPE, 43 Bd.du 11 Novembre 1918, 69622 Villeurbanne Cedex, France

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Various dialkyldibenzothiophenes containing methyl, ethyl, diisobutyl, and diisopropyl substituents in the fourth and sixth positions were synthesized and their reactivities compared over an $NiMo/Al_2O_3$ industrial catalyst. Studies were made in a batch reactor at 573 K and at a total pressure of 5 MPa. Kinetic studies and competitive reactions demonstrated that adsorption on the surface of the catalyst was not the rate-determining step for their transformation. Hydrodesulfurization was proposed to proceed via a network of parallel reactions after partial hydrogenation of one aromatic ring of the sulfur compound. Variations in the reactivities of the different dibenzothiophene derivatives are well correlated to the steric hindrance generated by the alkyl groups near the sulfur atom. Moreover, 4,6-diisopropyldibenzothiophene showed very low reactivity, and the steric effect led to the disappearance of desulfurization under our reaction conditions.

Key Words: **hydrodesulfurization; hydrogenation; alkyldibenzothiophenes; kinetics.**

INTRODUCTION

Crude oil typically contains about 1 wt% of sulfur; during combustion of fuels, SO_x, a major air pollutant, is emitted. Nevertheless, legislation should be in force by the year 2005, stipulating that diesel fuels cannot contain more than 0.05 wt% of sulfur. Due to increasingly restrictive legislation on the number of heteroatoms, especially sulfur, the production of "cleaner" distillate products is a major challenge for refiners.

Conventional catalytic hydrotreating processes have been used for many years to eliminate sulfur from distillates. These processes proved capable of removing the so-called "easy sulfur" compounds which include nonaromatic sulfur, thiophenes, and benzothiophenes. However, considerable amounts of "hard sulfur" compounds (0.2 to 0.3 wt%) are found in the diesel fraction, after conventional hydrodesulfurization (HDS) (1, 2). Considerable efforts have been made in past years to develop more active catalysts based on new supports or new active phases (3–5) and to improve catalytic processes by using two- or three-stage HDS processes (6, 7). However, until now none of them proved to be economically feasible for removing "hard sulfur" species from distillates. Recent findings on the HDS of polyaromatic sulfur compounds has been reviewed by Whitehurst *et al.* (8).

It is now well established that deep HDS is hindered mainly by one class of sulfur compounds, the alkyldibenzothiophenes (DBT), and more precisely by the β-substituted alkyldibenzothiophenes (1, 9–13). 4,6-Dimethyldibenzothiophene (4,6-DMDBT) has been recognized as a highly refractory sulfur-containing compound. This molecule has always been present in hydrotreated gas oils, even after hard HDS conditions (14). The synthesis of 4,6-DMDBT has been reported and its use as a model to improve the reactivity of HDS catalysts has been discussed. Kinetic investigations of the behavior of such alkyldibenzothiophene derivatives under HDS conditions have led to two contradictory explanations. The first hypothesis suggests that the transformation of 4-alkyl- and 4,6-dialkyldibenzothiophenes is limited by the adsorption step; it implies adsorption by the sulfur atom. In this case the alkyl groups sterically hinder adsorption (15, 16). The second proposal assumes that the adsorption of the dibenzothiophene compounds occurs via the π-electrons of the aromatic system. The alkyl groups do not hinder adsorption on the catalyst surface; instead the elimination step is assumed to be hindered by steric effects. Based on our previous studies, which included competitive experiments (17, 18), we assume that, after adsorption via an aromatic ring, the molecule is first hydrogenated to dihydrodibenzothiophene as postulated by Singhal *et al.* (19). This unstable intermediate can then be transformed via two pathways on similar catalytic sites by hydrogenation into tetrahydro- and hexahydrodibenzothiophene or by desulfurization according to an elimination mechanism resulting in biphenyl derivatives. Both propositions are being investigated by several groups.

Increasingly sophisticated analytical devices, especially gas chromatographs equipped with sulfur-specific

[1] To whom correspondence should be addressed. Fax: 33.4.72.44.53.99. E-mail: vrinat@catalyse.univ-lyon1.fr.

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detectors, have shown that other sulfur-containing molecules with a higher molecular mass are particularly resistant to classical HDS (20). Many research groups are determining the precise structure of these molecules and are trying to understand the reasons for their low reactivity. Following our previous investigations, we now report the synthesis of various alkyldibenzothiophenes (4,6-diethyldibenzothiophene, 4,6-diisobutyldibenzothiophene, and 4,6-diisopropyldibenzothiophene) that bear bulky substituents in both positions, which hinder the sulfur atom. We attemped to identify these structures in hydrotreated gas oils and we compared their reactivities in a batch reactor and over an industrial $NiMo/Al_2O_3$ hydrotreating catalyst.

SYNTHESIS OF VARIOUS 4,6-DIALKYLDIBENZOTHIOPHENES

General

Dialkyldibenzothiophenes are generally not commercially available, because they are not easily accessible. Very pure 4,6-DMDBT was prepared in a four-step procedure (25% global yield), starting with a coupling reaction of *o*-thiocresol and 2-bromo-3-nitrotoluene (21). However, to obtain a sufficient quantity of this compound, a more rapid and inexpensive method was developed by modifying the procedure published by Caubère *et al.* (22). Indeed, bislithiation of dibenzothiophene, which forms an insoluble species, was performed by adding tetramethylethylenediamine (TMEDA) to activate the metallating reagent, i.e., *n*-BuLi. Methylation was then performed using methyl iodide.

Caubère *et al.* (22) also tested this procedure for preparing higher homologues of 4,6-DMDBT. When ethyl iodide, instead of methyl iodide, was used with a larger amount of electrophile, 4,6-DEDBT was obtained but with a yield of only 40%. The successful preparation of 4,6-DEDBT was also achieved by performing the lithiation at position 6 of 4-ethyldibenzothiophene followed by alkylation using ethyl iodide (23, 24); the yield was 47%.

In the course of our studies on the synthesis of 4,6-DMDBT, we observed that the introduction of both methyl groups by two-step synthesis (i.e., lithiation and methylation of isolated 4-methyldibenzothiophene) results in 4-ethyldibenzothiophene as the major product. The lithiation of the methyl group is preferred to the transformation of the 6 position of 4-methyldibenzothiophene. This result is explained by better solubility of the dilithiated 4,6-DMDBT than of the 4,6-dilithiodibenzothiophene in cyclohexane. We thus decided to use this procedure to prepare various 4,6-dialkyldibenzothiophene derivatives, starting from 4,6-DMDBT and performing its dilithiation on both methyl groups.

We prepared 4,6-DEDBT (71% yield) starting from 4,6-DMDBT in the presence of *n*-BuLi, TMEDA, and methyl iodide. 4,6-Diisobutyldibenzothiophene (4,6-DiBuDBT) was analogously prepared in one step (60% yield) by metalation of 4,6-DMDBT and subsequent reaction with isopropyl iodide. The schemes of these syntheses are shown in Fig. 1.

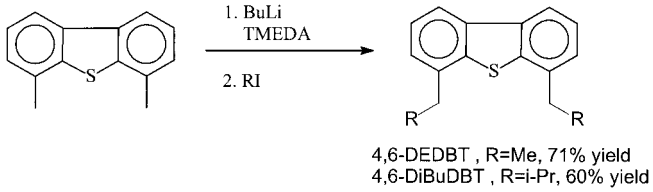

FIG. 1. Synthesis of 4,6-diethyl- and 4,6-diisobutyldibenzothiophene.

We were also interested in preparing a dibenzothiophene derivative that was sterically more hindered near the sulfur atom. We thus aimed to synthesize 4,6-diisopropyldibenzothiophene (4,6-DiPrDBT) by metalation and methylation of 4,6-DEDBT. This resulted in a mixture of numerous dialkylated dibenzothiophenes from which it was not possible to isolate the desired compound. Attempts to prepare 4,6-DiPrDBT by direct metalation and subsequent alkylation of DBT with isopropyl iodide failed. Numerous other electrophiles (e.g., acetone, *N,N*-dimethylformamide, dimethyl carbonate, trimethyl orthoacetate, or 1-acetylimidazole), precursors for the formation of the isopropyl substituent, were further tested. None of them led to the formation of the desired product, and only very poor conversion of DBT was observed.

It proved, however, possible to quench 4,6-dilithiodibenzothiophene with dry ice with a high yield (88%). The corresponding dicarboxylic compound was esterified and then reacted with methylmagnesium bromide to the tertiary diol. This product was dehydrated and hydrogenated with Pd/C under H_2 atmospheric pressure to 4,6-diisopropyldibenzothiophene with high purity (14% overall yield). A schematic representation of the synthesis is given in Fig. 2.

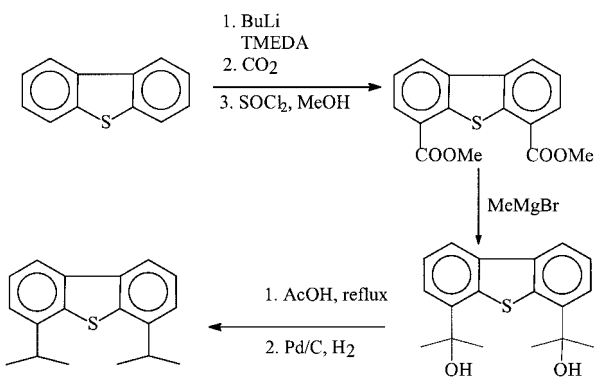

FIG. 2. Synthesis of 4,6-diisopropyldibenzothiophene.

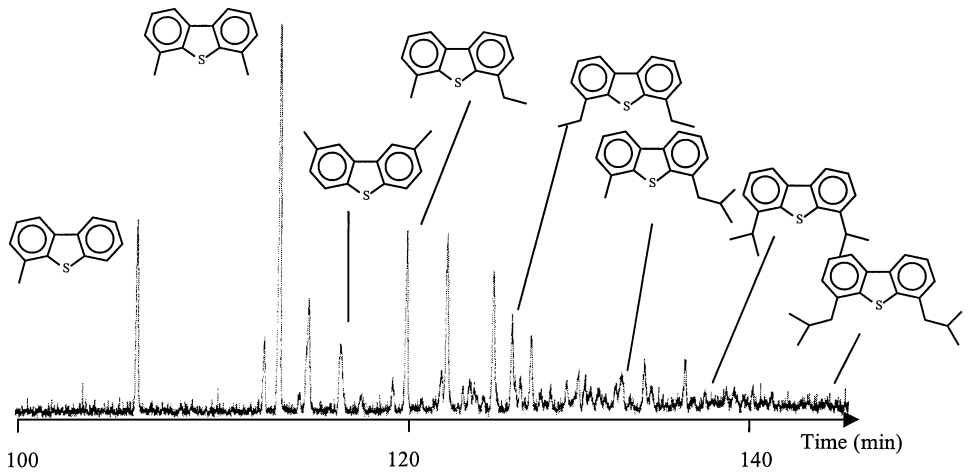

FIG. 3. Gas chromatography (Sievers detection) of a desulfurized gas oil: identification of some refractory compounds.

Sulfur derivatives obtained by these syntheses have been used, with the help of gas chromatography, as authentic samples to identify the structures of some refractory compounds contained in desulfurized gasoils (see Fig. 3). We then compared their reactivity in a batch reactor, on an industrial $NiMo/Al_2O_3$ hydrotreating catalyst.

Experimental

4,6-Dimethyldibenzothiophene (4,6-DMDBT) was prepared according to the method of Caubère *et al.* (22) after optimization by metalation and subsequent methylation of DBT.

4,6-Diethyldibenzothiophene (4,6-DEDBT) was prepared in one step (71% yield) by metalation and subsequent methylation of 4,6-DMDBT, as described in Fig. 1. First, 40.8 ml of BuLi was slowly added to a solution (10 ml) of TMEDA in 20 ml of anhydrous cyclohexane under stirring at 273 K. The mixture was stirred further for 45 min at 273 K and then diluted with 40 ml of anhydrous cyclohexane. At room temperature, 5.76 g of 4,6-DMDBT (27.17 mmol) was added, and the resulting reddish solution was refluxed for 3 h. Methyl iodide (5.36 ml) was then slowly added (1 h) at 258 K, and the mixture was stirred at room temperature overnight. The mixture was then hydrolyzed, and the organic phase was washed with saturated. NH_4Cl, and dried over magnesium sulfate. After purification in a silica column (CH_2Cl_2/cyclohexane 8/2) and recrystallization in isopropanol, 4.97 g of 4,6-DEDBT was obtained.

^{1}H NMR ($CDCl_3$): δ 1.4 (t, 6H), 3.0 (q, 4H), 7.2 (d, 2H), 7.4 (t, 2H), 8.0 (d, 2H). ^{13}C NMR ($CDCl_3$): δ 13.6, 28.1, 119.3, 124.8, 125.1, 136.3, 138.2, 138.6.

4,6-Diisobutyldibenzothiophene (4,6-DiBuDBT) was analogously prepared in one step (60% yield) by metalation of 4,6-DMDBT and subsequent reaction with isopropyl iodide (Fig. 1). First, 10.2 ml of BuLi was slowly added to a solution (2.5 ml) of TMEDA in 15 ml of anhydrous cyclohexane under stirring at 273 K. The mixture was stirred further for 45 min at that temperature and then diluted with 30 ml of anhydrous cyclohexane. At room temperature, 1.14 g of 4,6-DMDBT (5.4 mmol) was added, and the resulting reddish solution was refluxed for 3 h. Isopropyl iodide (2.15 ml) was then slowly added (1 h) at 258 K, and the mixture was stirred at room temperature overnight. The mixture was then hydrolyzed, and the organic phase was washed with saturated. NH_4Cl, and dried over magnesium sulfate. After purification in a silica column (CH_2Cl_2/cyclohexane 8/2) and recrystallization in isopropanol, 1.18 g of 4,6-DiBuDBT was obtained.

^{1}H NMR ($CDCl_3$): δ 0.9 (d, 12H), 2.15 (m, 2H), 2.7 (d, 4H), 7.15 (d, 2H), 7.35 (t, 2H), 7.9 (d, 2H). ^{13}C NMR ($CDCl_3$): δ 21.9, 30.2, 41.6, 124.8, 126.6, 128.2, 134.9, 138.2, 144.1.

4,6-Diisopropyldibenzothiophene (4,6-DiPrDBT) was prepared in five steps (14% overall yield, not optimized) starting from DBT (Fig. 2). First 108.8 ml of BuLi was slowly added to a solution (26.2 ml) of TMEDA in 50 ml of anhydrous cyclohexane under stirring at 273 K. The mixture was stirred further for 45 min at 273 K and then diluted with 100 ml of anhydrous cyclohexane. At room temperature, 8 g of DBT (43.5 mmol) was added, and the resulting reddish solution was refluxed for 3 h. Dry ice was then slowly added (1 h bubbling) at 258 K, and the mixture was stirred at room temperature overnight. The mixture was then hydrolyzed, and the organic phase was washed several times with water. The combined aqueous phases were washed with ether and then acidified with 1 N HCl, at which point the desired product precipitated. After filtration, the white crystals were washed with water and ether, and dried over P_2O_5. A total 10.45 g of 4,6-dicarboxydibenzothiophene was obtained with 88% yield.

Next, 5 g of 4,6-dicarboxydibenzothiophene (18.38 mmol) was stirred with 50 ml of thionyl chloride at 313 K for 10 h and then at room temperature for 12 h. The excess thionyl chloride was evaporated at lower pressure, and 15 ml of methanol and 10.2 ml of triethylamine were added to the residue. The mixture was refluxed for 4 h and stirred overnight at room temperature. The usual procedure (water/ethyl acetate) gave 2.87 g (52%) of 4,6-dicarboxymethyldibenzothiophene. This compound (2.5 g, 8.3 mmol) was dissolved in 80 ml of anhydrous THF, and the resulting suspension was cooled to 273 K. Next, 27.8 ml of MeMgBr (3 M in ether, 83 mmol) was added dropwise and the mixture was finally refluxed for 4 h. The usual procedure (water/ethyl acetate) gave 2.33 g (93%) of the desired diol. This compound was then quantitatively dehydrated in refluxing acetic acid with HCl. The corresponding unsaturated substituted dibenzothiophene was dissolved in 25 ml of a 1/1 mixture of $MeOH/CH_2Cl_2$, 650 mg of Pd/C (10 mol%) was added, and the mixture was stirred overnight under atmospheric H_2 pressure. After filtration and purification using silica gel chromatography (CH_2Cl_2/heptane 1/9), 533.8 mg of 4,6-DiPrDBT was obtained (33% yield).

^{1}H NMR ($CDCl_3$): δ 1.5 (d, 12H), 3.3 (m, 2H), 7.3 (d, 2H), 7.4 (t, 2H), 8.0 (d, 2H). ^{13}C NMR ($CDCl_3$): δ 22.7, 33.6, 119.3, 122.6, 125.0, 136.4, 138.1, 142.9.

KINETIC STUDY

Experimental Procedure

Materials. The catalyst used for the hydrodesulfurization of alkyldibenzothiophenes was an industrial $NiMo/Al_2O_3$ catalyst (Mo, 9 wt%; Ni, 2.4 wt%), provided as extrudates (bulk density, 0.71 g cm^{-3}; pore volume, 0.48 cm^3 g^{-1}; surface area, 185 m^2 g^{-1}). The extrudates were crushed, screened (80–125 μm), and then sulfided *ex situ* in an H_2–H_2S (15%) flow (4 l/h) at 673 K for 4 h before use.

Reactor and analytical. Studies were performed in a stirred slurry tank reactor (250 ml) operating in batch mode. The autoclave was equipped with a hollow-shaft, six-bladed magnetically driven turbine with four baffles on the wall to prevent vortex formation. The samples were collected through a tube ($\frac{1}{16}$-in. diameter); hydrogen was introduced through a pressure controller, which maintains a constant pressure during the course of the experiment. In each run, the autoclave was charged with 250 mg of reactant dissolved in 80 ml of dodecane. Freshly sulfided catalyst (400 mg) was added to the solution. The reactor was flushed with nitrogen and heated under stirring to reach the reaction temperature of 573 K; hydrogen was then introduced ($P_{tot} = 5$ MPa); this step was considered as the beginning of the reaction. Samples were periodically removed during the course of the reaction and analyzed by gas chromatography. GC analyses were performed using an apolar column (HP 5, 5% phenylmethylsilicone, 30 m $\times$ 0.53 mm) equipped with an FID detector. The different intermediates and products of the reaction were identified by GC/MS analyses. The reactant conversion and product yields were determined relative to an internal standard using hexadecane as the reference.

Control of the kinetic regime. Previous experiments were carried out to ensure the absence of intraparticle and interphase mass-transfer limitations. First the effects of the stirring rate and the weight and granulometry of the catalyst were controlled with a nonhindered molecule (DBT); the results indicated that the kinetic regime was established in all cases (25). Then, the internal diffusion of a more hindered compound (4,6-DiBuDBT) was studied by varying the granulometry (50–80 μm and 80–125 μm) of the catalyst. It appeared that there were no diffusional problems under our operating conditions when the mass of the catalyst was limited to 1 g and the stirring rate was fixed to at least 25 Hz.

Kinetic Calculations

Some experiments were performed with single products and others with equimolar mixtures of two compounds reacting in competition.

Hydrodesulfurization of a single compound. The results of a typical reaction course over time are presented for the transformation of 4,6-DEDBT in Fig. 4 . The initial rate of the transformation can be obtained from the slope of the 4,6-DEDBT disappearance curve at the origin. The yields of the different products can also be plotted against the conversion in order to determine the reaction scheme and the product selectivities (Fig. 5).

Hydrodesulfurization in competitive experiments. In competitive experiments, two compounds *A* and *B* compete

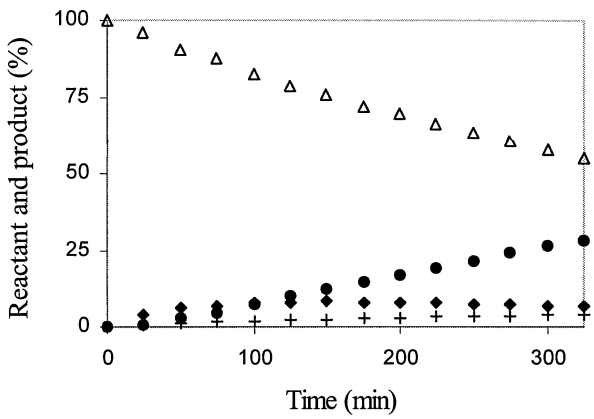

FIG. 4. Transformation of a single molecule (4,6-DEDBT): conversion versus time. Experimental conditions: 573 K, 5 MPa, NiMo catalyst; △, 4,6-DEDBT; +, alkylbiphenyl; ●, alkylcyclohexylbenzene; ◆, hydrogenated compounds.

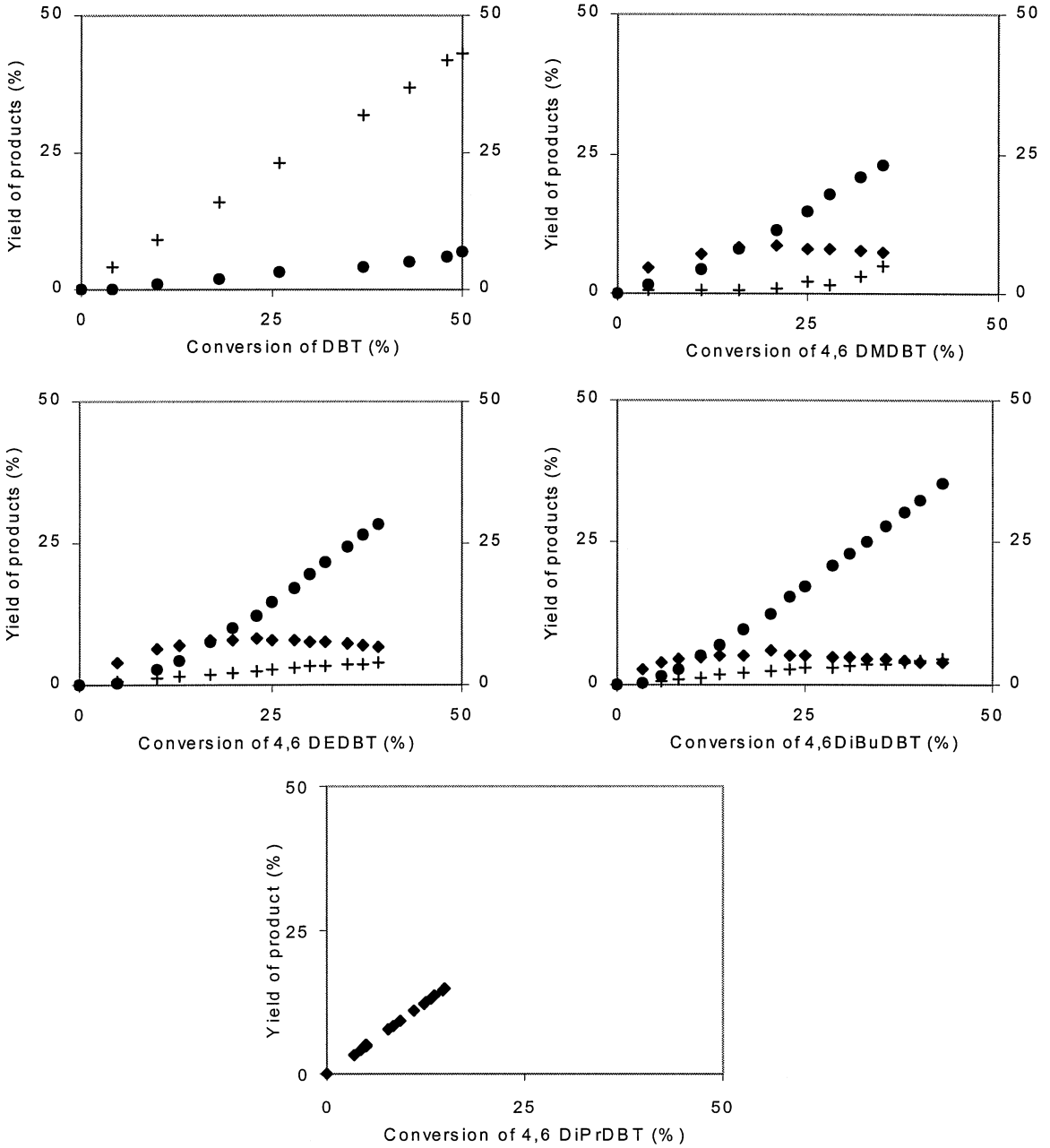

FIG. 5. Diagrams of yield versus conversion for the tranformation of DBT, 4,6-DMDBT, 4,6-DEDBT, 4,6-DiBuDBT, and 4,6-DiPrDBT (●, alkylcyclohexylbenzenes; ◆, hydrogenated compounds; +, alkylbiphenyls).

for adsorption on the same sites. R is the common reactant in the transformation of A and B.

The reactions can be schematized as follows:

$$R \rightleftharpoons \underline{R} \qquad \underline{A} + \underline{R} \xrightarrow{k_A} C$$

$$A \underset{k_{-1A}}{\overset{k_{1A}}{\rightleftharpoons}} \underline{A} \qquad \underline{B} + \underline{R} \xrightarrow{k_B} D,$$

$$B \underset{k_{-1B}}{\overset{k_{1B}}{\rightleftharpoons}} \underline{B}$$

where the underlined components (i.e., $\underline{A}$) correspond to the adsorbed species, k_{1i} and k_{-1i} represent the rate constant of adsorption and desorption, respectively, of component i and k_i the rate constant of the surface reaction of component i.

At the stationary state of $\underline{A}$ the balance between the formation and the disappearance of this species could be expressed by

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

The formation rate of C is

$$v_c = k_A[\underline{A}][\underline{R}], \quad [2]$$

where $[\underline{A}]$ can be expressed by

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

In this expression, $[i]$ represents the concentration of component i after a known reaction time, $[S]$ is the concentration of free active sites (unoccupied sites available for adsorption) at the surface, and $[\underline{R}]$ is the concentration of hydrogen adsorbed on the catalyst surface. In this expression no assumption was made about the mechanism of hydrogenation via molecular or dissociated hydrogen, though recent results (26, 27) strongly suggest that over sufide catalysts hydrogenation and hydrodesulfurization are performed with heterolytic dissociated hydrogen.

Similarly, $[\underline{B}]$ can be expressed by

$$[\underline{B}] = \frac{k_{1B}[B][S]}{k_{-1B} + k_B[\underline{R}]}. \quad [4]$$

If $[\underline{R}]$ is the same in both expressions, which means that the same hydrogen species are involved in the transformation of A and B, then the ratio is expressed by

$$\frac{v_C}{v_D} = \frac{d[A]}{d[B]} = \left(\frac{k_A k_{1A}[B]}{k_B k_{1B}[A]}\right)\left(\frac{k_{-1B} + k_B[\underline{R}]}{k_{-1A} + k_A[\underline{R}]}\right). \quad [5]$$

By integration of this equation, the reactivity ratio $R_{A/B}$ of the molecules A and B can be obtained (28–30):

$$\frac{\log[A]/[A_0]}{\log[B]/[B_0]} = \frac{k_A k_{1A}}{k_B k_{1B}}\left(\frac{k_{-1B} + k_B[\underline{R}]}{k_{-1A} + k_A[\underline{R}]}\right) = R_{A/B}. \quad [6]$$

The ratio $R_{A/B}$ at constant temperature does not depend on the initial composition of the mixture or on the extent of conversion. At relatively low hydrogen pressure, the surface reaction is the rate-determining step and $R_{A/B}$ can be expressed as a function of adsorption equilibrium constants and rate constants.

$$R_{A/B} = \frac{k_A K_A}{k_B K_B}, \quad [7]$$

with

$$K_i = \frac{k_{1i}}{k_{-1i}} \quad [8]$$

representing the adsorption equilibrium constant of compound i at the surface. We verified 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 (25). Moreover, a separate study of DBT indicated that, under our experimental conditions, the order of reaction relative to DBT was zero (25). That was also observed for 4,6-DMDBT and was assumed to be true for all other compounds.

Therefore, a comparison of the R values with the rate ratios k_A/k_B, calculated from the transformation of each product in separate experiments, enables the determination of the ratio K_A/K_B of the adsorption equilibrium constants.

Kinetic Results and Discussion

Transformation of the single molecules. The reaction products of the HDS of DBT were H_2S, biphenyl (BP), cyclohexylbenzene (CHB), and traces of partially hydrogenated sulfur-containing intermediates such as tetrahydro- and hexahydrodibenzothiophene. The same substituted analogues are observed for the substituted DBT. Moreover, the curves representing the yields of products versus the conversion of the studied molecule (Fig. 5) suggest that these alkyldibenzothiophenes are transformed according to two parallel routes in agreement with previous proposals in the literature reported for DBT, 4-methylDBT, and 4,6- DMDBT (8, 17, 19, 20). The first route, referred to as the direct desulfurization pathway (DDS), gives biphenyl derivatives. These desulfurized molecules are then slowly hydrogenated into cyclohexylbenzenes. The second pathway, referred to as the hydrogenation route (HYD), consists of a preliminary hydrogenation of one aromatic ring, giving tetrahydro- and hexahydrodibenzothiophene or analogues (HN). These intermediates can then be desulfurized.

From the curves in Fig. 5 we can determine the selectivities to all products; these appear to be related to the presence and size of the alkyl groups. In the case of DBT, the major product observed is BP, with CHB appearing significantly as a secondary product only at conversions higher than 30%. Only trace amounts of hydrogenated and nondesulfurized DBT are present. For 4,6-DMDBT, 4,6-DEDBT, and 4,6-DiBuDBT, the products result mainly from the hydrogenation pathway, leading to substituted cyclohexylbenzene and hydrogenated undesulfurized molecules; the concentration of biphenyl derivatives remains very low whatever the conversion. Selectivities calculated at 10% conversion are reported in Table 1, which also contains the relative rates of transformation.

TABLE 1

Catalytic Activity Results (Selectivities Are Calculated at 10% Conversion)

	Transformation rate (relative to DBT = 100)	S(BP), %	S(CHB), %	S(HN), %
DBT	100	90	10	0
4,6-DMDBT	15.9	9	30	61
4,6-DEDBT	11.9	13	29	58
4,6-DiBuDBT	6.3	10	40	50
4,6-DiPrDBT	2.3	—	—	100

For 4,6-DiPrDBT, the tendency of the reactant to be transformed according to the hydrogenation pathway is even more pronounced. Only hydrogenated products are observed, and no desulfurization is detected under our experimental conditions. These results confirm that substitutions of alkyldibenzothiophenes in the 4 and 6 positions significantly affect the direct desulfurization rate. The hydrogenation pathway appears to be less affected; therefore, the hydrogenation ability of the catalyst is of great importance in the conversion of such substituted compounds.

The initial tranformation rates of the different compounds were calculated from the slopes of the reactant transformation curves similar to the curve shown in Fig. 4. These values were compared to the DBT transformation rate, and ratios of these initial rates are given in Table 1. The rates decrease in the order

$$\text{DBT} > \text{4,6-DMDBT} > \text{4,6-DEDBT} > \text{4,6-DiBuDBT} > \text{4,6-DiPrDBT},$$

which confirms that HDS of the substituted DBTs is inhibited by the presence of alkyl groups at the carbon α to the sulfur atom. However, though 4,6-DMDBT (which is about 6 times less reactive than DBT) is generally considered to be a model compound for resistant sulfur molecules, it should be noted that the transformation of 4,6-DiPrDBT is more than 6 times slower than that of 4,6-DMDBT, and only hydrogenated products are observed. With regard to classical hydrodesulfurization, such a molecule would be considered to be a highly unreactive polyaromatic sulfur compound. A competitive study was carried out to determine the phenomena that might explain such inhibition.

Competitive experiments. Competitive studies were performed in order to determine whether the very low reactivities of some alkylated DBTs were due to difficulties with adsorption on a catalytic site or to differences in the surface reaction rates.

According to the theory of competitive hydrogenation, competitive experiments enable the determination of the reactivity ratio $R_{A/B} = k_A K_A / k_B K_B$. The rate constant ratio k_A/k_B can be easily derived from the r_i values (initial transformation rate of compound i) obtained under conditions at which a zero order relative to the hydrocarbon compounds is verified. This rate ratio, compared to the reactivity ratio obtained in competition, enables the calculation of the ratio K_A/K_B of the adsorption equilibrium constants of the two molecules. This calculation was made for various couples of alkyldibenzothiophenes using an equimolar mixture of the two compounds under standard experimental conditions ($NiMo/Al_2O_3$ catalyst, total pressure of 5 MPa, 573 K). Samples were periodically removed at increasing conversion to calculate the concentration of each reactant (A and B). The curves $\ln(A/A_0)$ versus $\ln(B/B_0)$ are given in Fig. 6, and the straight lines obtained demonstrate the validity of the competitive experimental approach and enable the calculation of the corresponding reactivity ratios $R_{A/B}$.

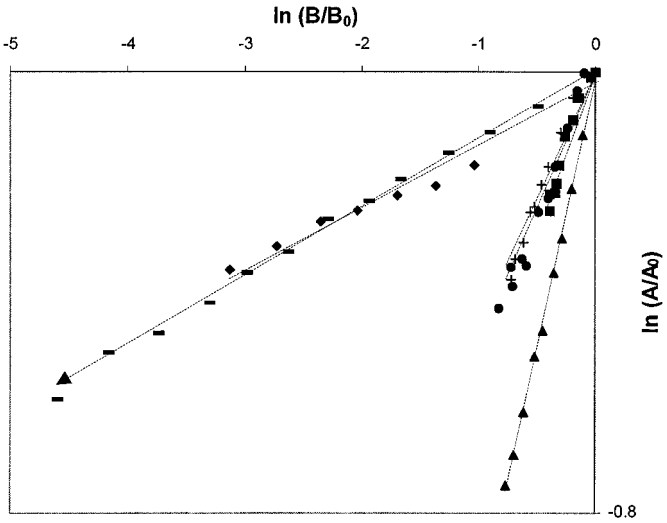

FIG. 6. $\ln(A/A_0)$ versus $\ln(B/B_0)$ obtained in competitive experiments. ◆, *A*, 4,6-DiBuDBT, *B*, DBT; ●, *A*, 4,6-DiBuDBT, *B*, 4,6-DEDBT; +, *A*, 4,6-DiPrDBT, *B*, 4,6-DMDBT; ■, *A*, 4,6-DiBuDBT, *B*, 4,6-DMDBT; ▲, *A*, 4,6-DEDBT, *B*, 4,6-DMDBT; —, *A*, 4,6-DMDBT, *B*, DBT.

The results in Table 2 show that, for most of the alkylDBT couples, except for experiments including the 4,6-DiPrDBT, the rate ratio k_A/k_B calculated from separate experiments is close to the reactivity ratio $R_{A/B}$ obtained from competitive experiments. Therefore, the adsorption equilibrium constants are almost the same for all studied molecules, suggesting that these compounds are adsorbed in the same way on the catalyst surface. Taking these results into account, adsorption by the sulfur atom is unrealistic. The constants of adsorption would otherwise be very different for molecules sterically hindered by alkyl groups around the sulfur atom. We can thus assume that adsorption of the DBT derivatives takes place via the π-electrons of the aromatic ring.

If the adsorption strength is not responsible for the difference in the reactivity of the various alkylDBT molecules,

TABLE 2

Results of Competitive Experiments

Products *A* and *B*	k_A/k_B	$R_{A/B}$	K_A/K_B
4,6-DMDBT/DBT	0.16	0.13	0.81
4,6-DEDBT/4,6-DMDBT	0.77	1	1.30
4,6-DiBuDBT/4,6-DEDBT	0.53	0.53	1
4,6-DiBuDBT/DBT	0.06	0.10	1.66
4,6-DiBuDBT/4,6-DMDBT	0.40	0.83	2.07
4,6-DiPrDBT/DBT	0.024	0.08	3.5
4,6-DiPrDBT/4,6-DMDBT	0.15	0.56	3.7

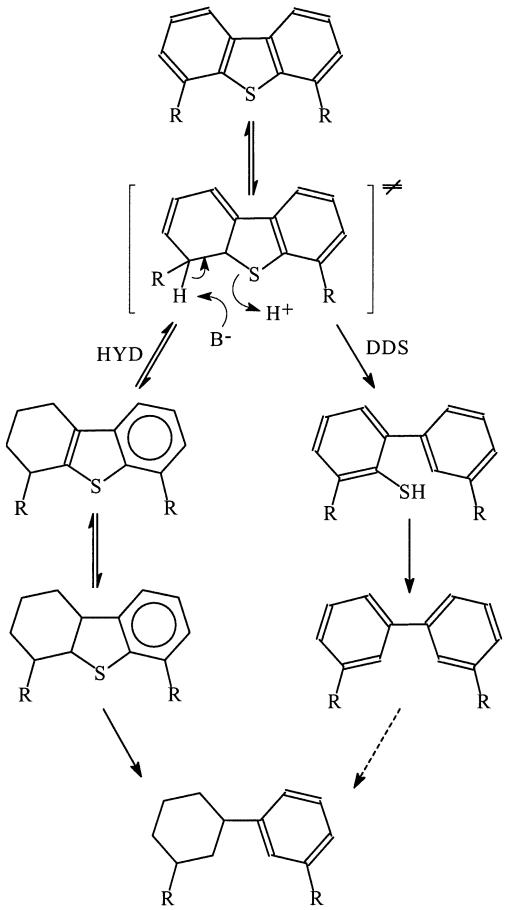

FIG. 7. Reaction scheme for the transformation of alkyl-DBT.

an explanation must be sought in the mechanism of evolution of the adsorbed species. For 4,6-DMDBT, 4,6-DEDBT, and 4,6-DiBuDBT, the decrease in the transformation rate is more pronounced with increasing size of the alkyl group, and these results seem to agree with the reaction scheme involving a partially hydrogenated intermediate, as previously proposed for the transformation of DBT, 4-MDBT, and 4,6-DMDBT (8, 17, 19, 20). This mechanism is shown in Fig. 7. Indeed, the lower reactivity would be related to the lower reaction rate for the C–S bond cleavage (elimination reaction) due to steric hindrance in the basic attack; this hindrance is generated by the alkyl group near the sulfur atom.

However, a detailed examination of the results obtained for the 4,6-DiPrDBT was interesting. This compound not only has the lowest reactivity of the various sulfur compounds studied, but competitive experiments indicate that, compared to DBT or 4,6-DMDBT, it also shows slightly stronger adsorption on the catalyst surface ($K_A/K_B = 3.5$). Therefore, this low reactivity and the absence of desulfurization (only hydrogenated products are observed) was explained by more pronounced steric hindrance in the basic attack. Though the number of carbon atoms of the alkyl groups of this compound is lower than for 4,6-DiBuDBT, the steric hindrance generated near the sulfur atom is more important. The tertiary carbon atom is closer to the sulfur in the isopropyl compound compared to the isobutyl compound. Such evolution of the transformation rates with the size as well as with the nature of the alkyl substituents is in good agreement with the proposed mechanism.

CONCLUSION

Kinetic studies of individual compounds and competitive experiments with mixtures have proved that the drastic decrease in the global reaction rate of alkyl- substituted dibenzothiophenes, compared to DBT, is due not to adsorption but to steric hindrance in the elimination reaction involved in the C–S bond scission. Such inhibition is increasingly pronounced on going from 4,6-DMDBT to 4,6-DEDBT and to 4,6-DiBuDBT, in agreement with the increase in the size of the substituent.

In the case of 4,6-DiPrDBT, the steric effect leads to the elimination of the desulfurization under the chosen conditions. This compound might be considered as a better model of highly unreactive polyaromatic sulfur, since its transformation rate is about 2 orders of magnitude lower than that of dibenzothiophene.

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