JOURNAL OF CATALYSIS 61, 115–127 (1980)

Hydrodesulfurization of Oxidized Sulfur Compounds in Benzothiophene, Methylbenzothiophene, and Dibenzothiophene Series over $CoO-MoO_3-Al_2O_3$ Catalyst

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Received May 23, 1978; revised April 9, 1979

Hydrodesulfurization experiments were carried out with a sulfided $CoO-MoO_3-Al_2O_3$ catalyst at various elevated pressures (30 to 70 atm) and temperatures (200 to 300°C) under stirred batch reactor conditions. The reactants were hydrogen and pure sulfur compounds including dibenzothiophene, benzothiophene and its methyl derivatives, and their oxidized products, sulfoxides and sulfones. In the case of dibenzothiophene the reaction is the C–S bond scission without any observed hydrogenation of the aromatic ring. For the S-oxidized compounds a deoxygenation takes place first and the sulfide reacts as before. For benzothiophene (BT) and its methyl derivatives there is first a hydrogenation of the C_{2-3} thiophenic double bond and then desulfurization leading to ethylbenzene derivatives. For the sulfoxides a deoxygenation takes place first but for the sulfones (BTO_2) as for the sulfide the hydrogenation is operative. Methyl substitution leads to a decrease in the rate of the hydrogenation step in the BT and BTO_2 series. A correlation, related to the overall aromaticity of the system, between the rate constants and the vertical ionization potential of the molecules, suggests that electronic effects may be preponderant.

INTRODUCTION

Catalytic hydrodesulfurization is economically a very important process because of the increasing demand for fuels containing the smallest possible amounts of sulfur as well as for the protection of environment (*1*). In these fuels most of the sulfur compounds are thiophenic with predominantly benzo and dibenzothiophene derivatives, but except for thiophene itself there have been relatively few studies of their hydrodesulfurization (*2*).

According to these results two processes can take place depending upon the reaction conditions (temperature, hydrogen pressure, type of catalyst, operative conditions, etc.): hydrogenation and hydrogenolysis.

For dibenzothiophene hydrogenation of an aromatic ring adjacent to the thiophenic one has been proposed by Cawley (*3*) and Urimoto and Sakikawa (*4*). But more recently Bartsch and Tanielian (*5*) showed that the first step is the breaking of the C–S bond, resulting in the formation of biphenyl.

The same kind of duality exists for benzothiophene itself and its derivatives. Even if the principal product formed during the hydrodesulfurization process is the ethylbenzene it can come either from the styrene due to C–S bond breaking, as proposed by Bartsch and Tanielian (*5*) and Furimsky and Amberg (*6*), or from 2,3-dihydrobenzothiophene due to an initial hydrogenation of the thiophenic part of the molecule, as proposed by Cawley (*3*), Givens and Venuto (*7*, Schuit and Gates (*8*), and De Beer *et al.* (*9*).

More recently Daly (*10*), working at higher pressure and temperature, suggested that the hydrodesulfurization of benzothiophene may involve two different reaction mechanisms: either hydrogenation or hydrogenolysis.

A great number of other questions remain

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0021-9517/80/010115-13$02.00/0

unanswered, such as the nature of chemisorption, the mechanism of C–S bond rupture, and the nature of the active sites (*11*). We have therefore chosen to study the role played by the sulfur atom which, depending upon its various oxidation states, can influence the aromatic character of the entire molecule as shown in thiophenic series (*12*). In fact, the transformation of the sulfur compounds to their corresponding oxides (sulfoxide or sulfone) should provide insight into the desulfurization reaction since the electronic configuration of the sulfur has been significantly modified.

We chose to study both dibenzothiophene and unsymmetrical molecules such as benzothiophene and its methyl derivatives where the two processes, hydrogenation and hydrogenolysis, can become kinetically competitive.

Since industrial reactions are conducted at pressures greater than 50 atm, it was of interest to study the hydrodesulfurization reaction at elevated hydrogen pressure under stirred batch reactor conditions.

EXPERIMENTAL

Catalyst

The catalyst was Procatalyst HR 103, a desulfurization catalyst used industrially, which has the following composition (wt%): CoO 2.8; MoO_3 13.5; NiO < 0.03; SiO_2 2.8; and Al_2O_3 80.9. This catalyst was sulfurized using a fluidized bed technique with a gas mixture composed of 15% H_2S and 85% H_2 by volume; the operational pressure was 1 atm; the rate of gas flow was 4 liters/h per 100 g of catalyst; and the initial temperature was 100°C. It was increased from 100 to 400°C during 24 h and then held at 400°C for 24 h (*13*).

Reactants and Analysis

1. Benzothiophene and dibenzothiophene were Fluka products whose purity was verified by gas chromatography; mp 30–32 and 94–97°C, respectively.

2-Methylbenzothiophene was prepared according to the method of Shirley and Cameron (*14*) by metalation of benzothiophene with *n*-butyllithium followed by methylation with methylparatoluene sulfonate; mp 47–48°C.

3-Methylbenzothiophene and 2,3-dimethylbenzothiophene were synthesized according to the method described by Chapman *et al.* (*15*) by cyclization of phenylthioacetone for the first and 3-phenylthio-2-butanone for the second.

3-Methylbenzothiophene, bp 76–79°C/ 3 mm.
2,3-Dimethylbenzothiophene, bp 119–122°C/12 mm (lit. bp 122–124°C/13 mm (*16*)).

2. The sulfoxides were obtained by oxidation of the corresponding sulfides with *m*-chloroperbenzoic acid in chloroform at 0°C or with *tert*-butyl hypochlorite at −70°C in methanol (*17*). The reaction products were separated by chromatography on silica.

1-Oxodibenzothiophene, mp 186–188°C (lit. mp 185–187°C (*18*)).
3-Methyl-1-oxobenzothiophene, mp 78–80°C.
2,3-Dimethyl-1-oxobenzothiophene, mp 115–116°C.

3. The sulfones were prepared by oxidation of the sulfides with hydrogen peroxide in acetic acid (*19*). Generally, the sulfones were isolated by crystallization.

1,1-Dioxodibenzothiophene, mp 229–231°C (lit. mp 233–234°C (*19*)).
1,1-Dioxobenzothiophene, mp 143–145°C.
2-Methyl-1,1-dioxobenzothiophene, mp 104–105°C.
3-Methyl-1,1-dioxobenzothiophene, mp 144–146°C.
2,3-Dimethyl-1,1-dioxobenzothiophene, mp 146–148°C.

4. The 2,3-dihydrobenzothiophenes were prepared by hydrogenation of the corresponding sulfones on a 10% Pd/C catalyst in ethyl alcohol to obtain the dihydro-

genated sulfones which, when treated with aluminum–lithium hydride in ether, give the 2,3-dihydrogenated sulfides (*20*).

2,3-Dihydro-1,1-dioxobenzothiophene, mp 90–92°C.
2,3-Dihydrobenzothiophene, bp 94–96°C/5 mm (lit. bp 93°C/6 mm (*21*)).
2,3-Dihydro-2-methyl-1,1-dioxobenzothiophene, mp 113–114°C.
2,3-Dihydro-2-methylbenzothiophene, bp 129–130°C/28 mm.
2,3-Dihydro-3-methyl-1,1-dioxobenzothiophene, mp 55–56°C (lit. mp 58–58.5°C (*22*)).
2,3-Dihydro-3-methylbenzothiophene, bp 125–126°C/25 mm (lit. bp 101.5–102°C/8 mm (*22*)).
2,3-Dihydro-2,3-dimethyl-1,1-dioxobenzothiophene, mp 72–74°C (lit. mp 74.5–75°C (*22*)).
2,3-Dihydro-2,3-dimethylbenzothiophene, bp 134–135°C/25 mm (lit. bp 129–130°C/20 mm (*22*)).

5. The 1,1-dioxo-4*a*,7*a*-sulfinyl-4,7,8,9-tetrahydrobenzothiophene (sesquioxide of benzothiophene) was obtained by oxidation of thiophene with perbenzoic acid (*35*); mp 181–182°C.

6. The styrene, methylated derivatives, and alkylbenzenes and dodecane were Fluka products.

The products were analyzed by gas chromatography on a Varian Series 1200 flame ionization instrument, equipped with either an OV-17 (50% phenylsilicone) or an SE-30 (methylsilicone) column. The following separation conditions were used for the sulfides, the oxidized products, and the obtained hydrocarbons: injector 270°C, detector 300°C, and temperature programming from 70° to 270°C at 6°C/min. The gas carrier was nitrogen.

Desulfurization Unit

The apparatus used for the kinetic studies was an agitated autoclave with a 0.5-liter capacity, allowing operations up to 500°C and 200 atm. This autoclave was equipped with sample inlets, heated by an external oven, and could be agitated at different speeds by mechanically changing pulleys. The characteristics of this batch operation have been studied by Barret (*23*).

Operation

The sulfur compounds and the catalyst were introduced into the reactor in a dodecane solution. The autoclave was closed and inserted into the oven. Air was removed by purging with nitrogen at 5 atm pressure. The temperature was increased at atmospheric pressure, and care was taken not to exceed the required temperature because of the high inertia of the oven. Hydrogen was introduced at time zero at 10 to 15°C below the working temperature. Agitation was stopped for 1 to 2 min to withdraw samples. Throughout the experiments the sulfur content of the reactant was kept at 0.3% of the weight of the charge.

Kinetic Analysis and Calculations

The reaction orders were determined from experimental curves by curve fitting (and simulation) using a HP 9820 A computer equipped with a 9826 A tracing table.

For a kinetic consecutive scheme

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B} \xrightarrow{k_2} \mathrm{C} \xrightarrow{k_3} \mathrm{D}$$

with an order of 1 for the starting material, it is possible to obtain the individual rate constants by resolving the system of equations:

$$(A) = (A_0)e^{-k_1t},$$

$$(B) = \frac{k_1(A_0)}{k_2 - k_1}(e^{-k_1t} - e^{-k_2t}),$$

$$(C) = k_1k_2(A_0)\left[\frac{e^{-k_1t}}{(k_2 - k_1)(k_3 - k_1)} + \frac{e^{-k_2t}}{(k_1 - k_2)(k_3 - k_2)} + \frac{e^{-k_3t}}{(k_1 - k_3)(k_2 - k_3)}\right].$$

The computer program uses an iteration

method starting with the initial concentration (A_0) of the species A, the instantaneous values of (A) (B) (C) at each time t, and an approximate value of the three rate constants given by curve fitting (and simulation).

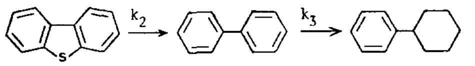
In the case of zero-order reactions, the experimental constants have been divided by the initial concentration to obtain a rate constant (in min^{-1}).

The experimental values are the mean of at least three independent runs.

RESULTS

(*1*) *Dibenzothiophene Series*

Sulfides. The primary products obtained from dibenzothiophene (DBT) were biphenyl (BP) and phenylcyclohexane (PCH) according to the following scheme.



The experimental results (concentration versus time as indicated in Fig. 1) have been studied by curve fitting and are satisfactorily accounted for by a zero-order reaction in DBT.

TABLE 1

Influence of Temperature on Rate Constants in Dibenzothiophene Series[a]

Reagent	T (°C)	10^4k_1 (min^{-1})	10^4k_2 (min^{-1})	10^4k_3 (min^{-1})
DBT[b]	200		0.2	—
	230		1.2	—
	250		4	0.5
	280		15	—
	300		37	17
DBTO	200	110	—	—
	230	320	—	—
	250	550	3	—
	280	810	—	—
	300	850	30	25
$DBTO_2$	200	170	—	—
	230	250	—	—
	250	370	3	—
	280	370	—	—
	300	400	47	25
BP[b]	300			2

[a] $P_{H_2} = 50$ atm.

[b] The experimental constants have been divided by the initial concentration to obtain a rate constant in min^{-1}.

The rate constants k_2 for several temperatures are listed in Table 1 and an apparent activation energy of approximately 28 kcal/mole has been determined, in agreement with the results of Rollmann (*24*) who found a value of 36 kcal/mole.

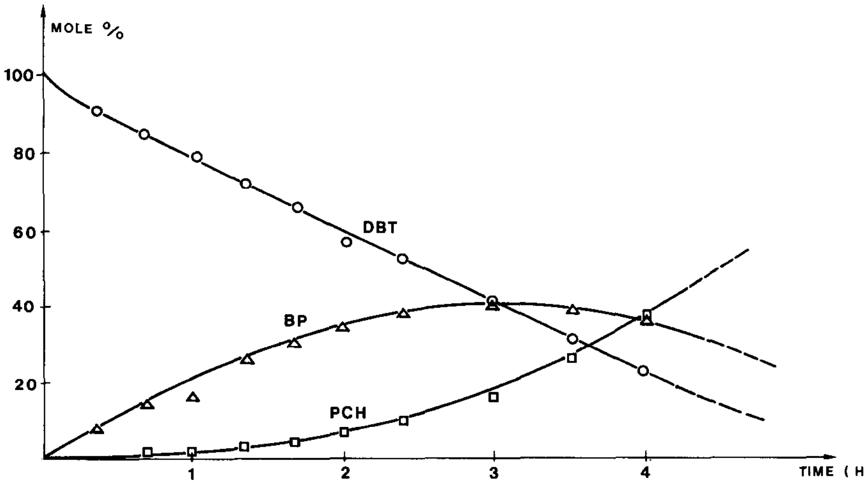


FIG. 1. Desulfurization of dibenzothiophene (DBT). T = 300°C; P_{H_2} = 50 atm; wt% of S based on charge = 0.3.

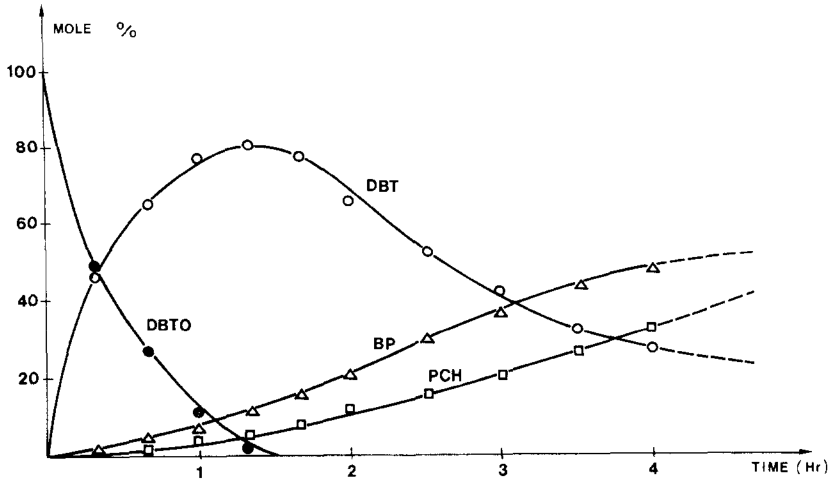
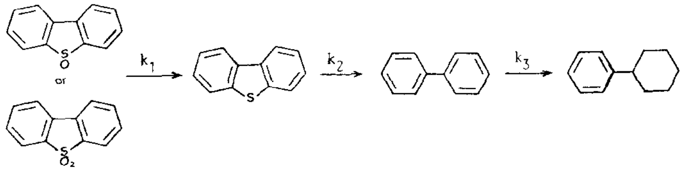


FIG. 2. Desulfurization of 1-oxodibenzothiophene (DBTO). $T = 300°C$; $P_{H_2} = 50$ atm; wt% of S based on charge = 0.3.

Sulfoxide and sulfone. In all cases, starting from either the sulfoxide (DBTO) or the sulfone ($DBTO_2$), the first step corresponds to formation of the sulfide according to the following scheme.



We present in Figs. 2 and 3 the characteristic results of the oxidized products, DBTO as well as $DBTO_2$. In these cases starting from one or the other of these derivatives, consecutive first-order processes

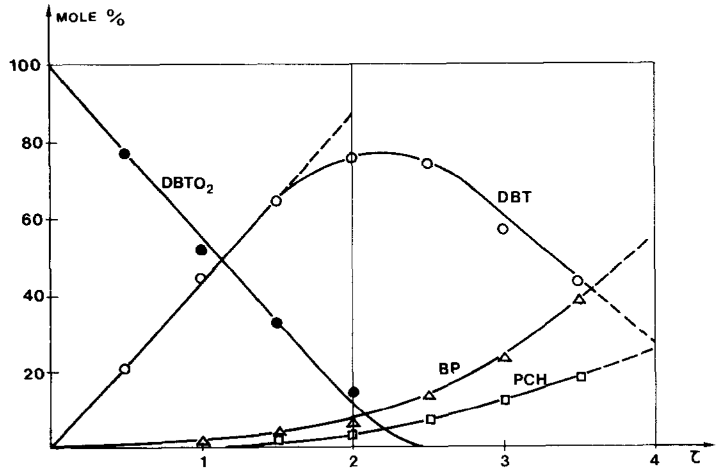


FIG. 3. First-order consecutive process in the case of 1,1-dioxodibenzothiophene ($DBTO_2$). $\tau = (2n_{DBT} + 4n_{BP} + 7n_{PCH})/n^0_{DBTO_2}$, where n_i = molar fraction of species i at time t. $T = 300°C$; $P_{H_2} = 50$ atm.

TABLE 2

Influence of Hydrogen Partial Pressure on Rate Constants in Dibenzothiophene Series[a]

Reagent	Pressure (atm)	10^4k_1 (min^{-1})	10^4k_2 (min^{-1})	10^4k_3 (min^{-1})
	30		35	14
DBT[b]	50		37	17
	70		32	20
	30	380	46	26
$DBTO_2$	50	400	47	25
	70	430	49	19

[a] T = 300°C and wt% of S based on charge = 0.3.

[b] The experimental constants have been divided by the initial concentration to obtain a rate constant in min^{-1}

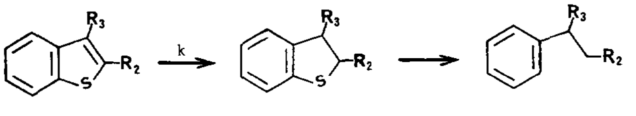
are operative according to an exponential decrease of the initial material. The kinetic rate constants are therefore readily obtained by curve fitting using the calculation method described under Experimental.

Effect of hydrogen pressure. Increasing the pressure gives better desulfurization yields. Our experiments have been carried out with a constant weight of catalyst and a constant molar concentration of sulfur (0.3 wt%). The values of the rate constants, calculated as previously mentioned, are indicated in Table 2. Within experimental error (±5%), the results show that the kinetic order with respect to hydrogen is close to zero under our high-pressure conditions, indicating that saturation of the catalytic surface is essentially complete in our liquid-phase experiments.

(*2*) *Benzothiophene Series*

Sulfides. From the desulfurization results shown in Figs. 4 and 5 (concentration versus time curves) we determined the kinetics to be zero order in the reactant with either benzothiophene (BT) or DHBT. The only products obtained from BT are DHBT and ethylbenzene (EB). On the other hand, starting from DHBT there is no formation of BT. These results show the irreversible character of the BT → DHBT reaction under our conditions, contrary to what had been postulated under vapor-phase conditions (*6, 7*).

The behavior of methyl-substituted benzothiophenes in the 2 and/or 3 positions is the same as that of BT itself in accordance with the consecutive kinetic process presented in the following scheme.



1a R_2=R_3=H (BT)	1b R_2=R_3=H (DHBT)	1c R_2=R_3=H (EB)
2a R_2=CH_3; R_3=H	2b R_2=CH_3; R_3=H	2c R_2=CH_3; R_3=H
3a R_2=H; R_3=CH_3	3b R_2=H; R_3=CH_3	3c R_2=H; R_3=CH_3
4a R_2=R_3=CH_3	4b R_2=R_3=CH_3	4c R_2=R_3=CH_3

Rate constants for the hydrogenation step have been determined (Table 3). Substitutions in the 2 and/or 3 positions decrease the rate as expected and will be discussed below.

The apparent activation energies have been determined as follows (kcal/mole): benzothiophene, 25; 3-methylbenzothiophene, 32; and 2,3-dimethylbenzothiophene, 37. They are of the same order of magnitude as those found previously in these series (*10, 24*).

Sulfoxides. As we have previously shown the sulfoxide of BT is not isolable (*17*) and can only be considered as a reaction intermediate in the oxidation process.

However the substituted benzothiophenes give stable sulfoxides whose hydrodesulfurization results are presented in Fig. 6. The analysis of the curves is in accord-

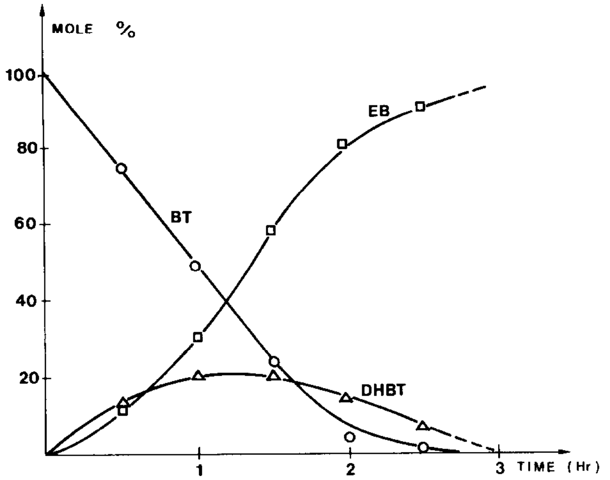
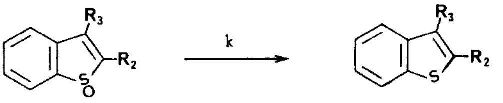


FIG. 4. Desulfurization of benzothiophene (BT). T = 250°C; P_{H_2} = 50 atm; wt% of S based on charge = 0.3.

ance with a consecutive kinetic process. The order in reactant is 1 in the first step which corresponds to a deoxygenation reaction. The hydrogenation takes place afterward in the same way as with BT according to the following scheme.



5 R_2=H; R_3=CH_3
6 R_2=R_3=CH_3

3a R_2=H; R_3=CH_3
4a R_2=R_3=CH_3

Rate constants of this deoxygenation reaction, reported in Table 4, have been determined by curve fitting according to the method indicated under Experimental.

Sulfones. From the desulfurization results presented in Figs. 7 and 8 (molar percentage versus time curves), we determined a kinetic order of 1 in the reactant whenever the starting material was BTO_2 or $DHBTO_2$. As found previously for BT and substituted BT, the first step of the whole process is a hydrogenation reaction of the double bond located between carbon atoms 2 and 3. The next step is a deoxygenation reaction followed by hydrodesulfurization. The behav-

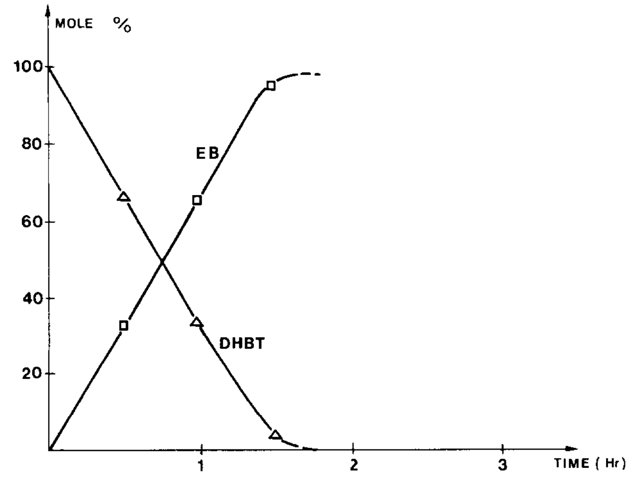


FIG. 5. Desulfurization of 2,3-dihydrobenzothiophene (DHBT). T = 250°C; P_{H_2} = 50 atm; wt% of S based on charge = 0.3.

TABLE 3

Influence of Temperature on the First Step of the Conversion of Sulfides in Benzothiophene Series[a]

Reagent	No.	T (°C)	10^4k[b] (min^{-1})	E (kcal/mole)
BT	1a	200	4.1	
		230	28	
		250	84[c]	25
		280	240	
		300	470	
2-MeBT	2a	250	31	
3-MeBT	3a	200	0.6	
		230	6	
		250	15	32
		280	82	
		300	220	
2,3-diMeBT	4a	200	0.1	
		230	2.1	
		250	9	37
		280	37	
		300	100	

[a] P_{H_2} = 50 atm. E = Activation energy.

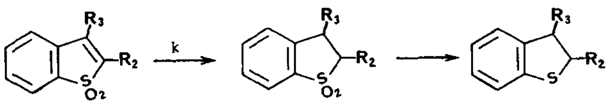
[b] The experimental constants have been divided by the initial concentration to obtain a rate constant in min^{-1}.

[c] In the case of DHBT at 250°C the rate constant corresponding to the formation of EB is of 110.10^{-4} min^{-1}.

ior of the sulfones is thus different from that of the sulfoxides.

On the other hand, with DHBTO$_2$ as the reactant, there is no dehydrogenation process and the reaction BTO$_2$ → DHBTO$_2$ is irreversible under our conditions.

These results were confirmed using 2- and/or 3-methylderivatives. The overall reaction is then a consecutive kinetic process as presented in the following scheme.



7a R$_2$=R$_3$=H (BTO$_2$)	7b R$_2$=R$_3$=H (DHBTO$_2$)	1b R$_2$=R$_3$=H (DHBT)
8a R$_2$=CH$_3$; R$_3$=H	8b R$_2$=CH$_3$; R$_3$=H	2b R$_2$=CH$_3$; R$_3$=H
9a R$_2$=H; R$_3$=CH$_3$	9b R$_2$=H; R$_3$=CH$_3$	3b R$_2$=H; R$_3$=CH$_3$
10a R$_2$=R$_3$=CH$_3$	10b R$_2$=R$_3$=CH$_3$	4b R$_2$=R$_3$=CH$_3$

Rate constants of the first step, reported in Table 5, were also determined by curve fitting. The reactivity is increased in these series relative to the sulfides by a factor of about 10 with a corresponding decrease in the apparent activation energy by a factor of about 3.

The presence of the methyl group, however, decreases the reactivity to a lesser extent for the sulfones and the rate-retarding effect of the 3-methyl substituent is now less than that of the 2-methyl substituent. These results will be discussed below.

Sesquioxide. To confirm the different behavior of the two oxidized products, we used the sesquioxide of thiophene as a model for a possible competition reaction. This compound has the advantage of possessing both a sulfinyl and a sulfonyl group and two unconjugated double bonds. Unfortunately, it is unstable under the experi-

TABLE 4

Influence of Temperature on the First Step of the Conversion of Sulfoxides in Benzothiophene Series[a]

Reagent	No.	T (°C)	10^4k (min^{-1})
3-MeBTO	5	200	530
		230	740
		250	870
		280	1660
		300	2300
2,3-diMeBTO	6	200	460
		230	690
		250	810
		280	1150
		300	1400

[a] P_{H_2} = 50 atm.

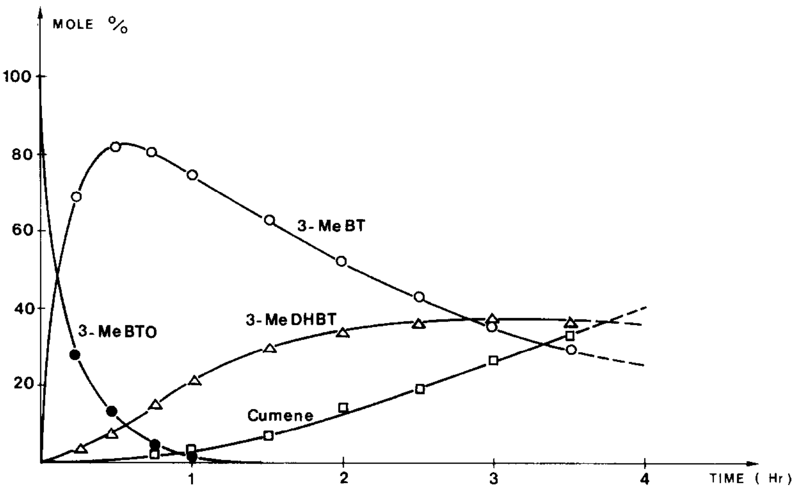
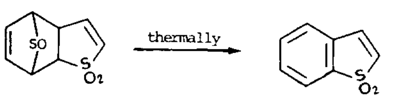


FIG. 6. Desulfurization of 3-methyl-1-oxobenzothiophene (3-MeBTO). $T = 250°C$; $P_{H_2} = 50$ atm; wt% of S based on charge = 0.3.

mental conditions, giving the sulfone of benzothiophene.



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DISCUSSION

Our results show that although there are many similarities in the behavior of these compounds, there are substantial differences as well, depending on the series (benzothiophene or dibenzothiophene) and the oxidation state of the sulfur.

In the dibenzothiophene series, we find the reaction to be zero order in DBT. This result, which is different from that given by Wilson *et al.* (*25*) as well as by Bartsch and Tanielian (*5*), who found an order of 1, is suggested to be due to a difference in reaction conditions (temperature, pressure, liquid phase, preparation of catalyst, etc.). The finding of a consecutive reaction scheme for the hydrodesulfurization of dibenzothiophene, leading first to biphenyl and then to phenylcyclohexane, confirms that hydrogenation of the aromatic ring is not necessary for rupture of the C–S bond (*5, 9*) which appears to be the slow step of the reaction (*24, 34*). These results, and the fact that under our conditions (Table 2) the hydrogenation of biphenyl is possible, are in agreement with the results of Hoog (*26*) and Landa and Mrnkova (*27*), who found biphenyl and its compounds partially hydrogenated, but not with the results of Obolentsev and Mashkina (*28*) who sug-

TABLE 5

Influence of Temperature on the First Step of the Conversion of Sulfones in Benzothiophene Series[a]

Reagent	No.	T (°C)	10^4k (min^{-1})	E_{app} (kcal/mole)
BTO_2	7a	200	200	10
		230	500	
		250	920	
		280	1050	
		300	1300	
2-MeBTO_2	8a	250	730	
3-MeBTO_2	9a	200	460	6
		230	650	
		250	810	
		280	1140	
		300	1400	
2,3-diMeBTO_2	10a	200	180	9
		230	240	
		250	290	
		280	680	
		300	990	

[a] $P_{H_2} = 50$ atm.

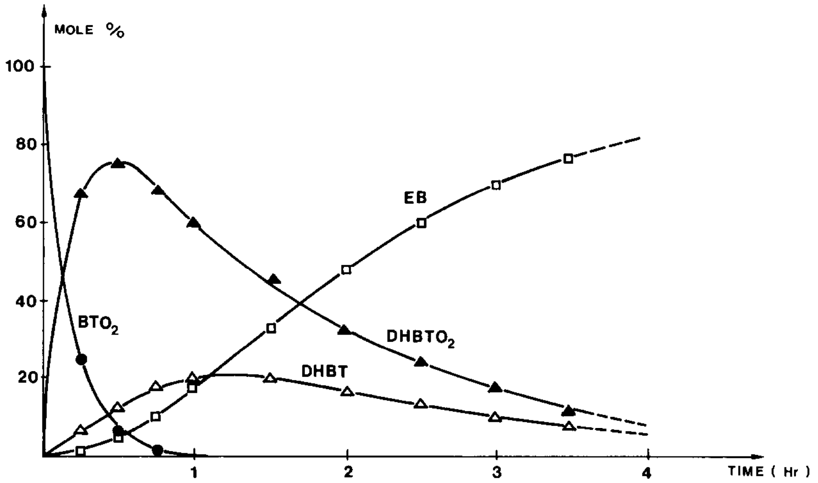


FIG. 7. Desulfurization of 1,1-dioxobenzothiophene (BTO_2). T = 250°C; P_{H_2} = 50 atm; wt% of S based on charge = 0.3.

gested that a pressure of 40 atm is not sufficient to saturate the biphenyl obtained by hydrogenolysis of dibenzothiophene.

For the sulfoxide (DBTO) and the sulfone ($DBTO_2$) we find a first-order consecutive reaction with a common first step of deoxygenation and transformation to the sulfide.

It seems thus that the modification of the *d* sulfur orbitals and consequently the aromatic character of the molecule have no observable effect on the hydrodesulfurization of symmetric molecules such as dibenzothiophene since the reaction of hydrodesulfurization must take place through dibenzothiophene itself.

In the benzothiophene series, the individual steps of the hydrodesulfurization depend on the oxidation state of the sulfur:

—for the sulfides (BT and methyl derivatives) there is first hydrogenation of the double bond and then desulfurization;

—for the sulfoxides, deoxygenation takes place first followed by the hydrogenation of the double bond and then desulfurization;

—for the sulfones, as in the case of sulfides, the first step is the hydrogenation of the double bond followed by deoxygenation and then desulfurization.

As in the case of the dibenzothiophene series, we found a zero order in BT and DHBT, which is in contrast to the data in the literature. In addition, for the methylbenzothiophenes, we did observe neither dealkylation nor methyl migration reactions as was found by Givens and Venuto (*7*). Furthermore, contrary to the results of these authors (*7*) and to those of Furimsky and Amberg (*6*) in the hydrodesulfurization of 2,3-dihydrobenzothiophene, we found no dehydrogenation and thus no formation of benzothiophene. These inconsistencies may be due to differences in operating conditions (temperature, pression, preparation of the catalyst, concentration of sulfurized reactant which may modify the percentage of sulfur of the catalyst, etc.).

Our results, however, permit us to confirm that hydrogenation of the aromatic ring is not necessary for cleavage of the C–S bond.

For the sulfoxides and the sulfones, we find a kinetic order of 1 in the reactant with a difference in behavior of the sulfoxides and sulfones which is probably due to the more aromatic character of the sulfoxides

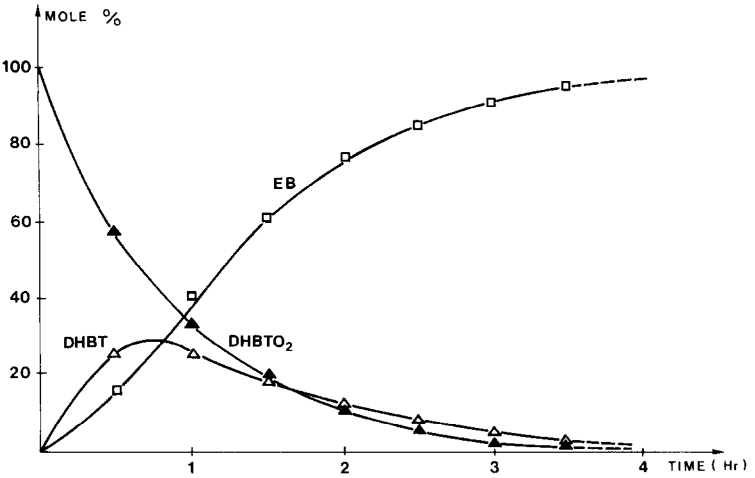


FIG. 8. Desulfurization of 2,3-dihydro-1,1-dioxobenzothiophene ($DHBTO_2$). $T = 250°C$; $P_{H_2} = 50$ atm; wt% of S based on charge = 0.3.

as can be shown by the chemical shifts in ^{13}C NMR studies in these series (*29*). The C_{2-3} bond has more double-bond character in the sulfones than in the sulfoxides. This explanation also applies to the slowest rate of the hydrogenation reaction of the sulfides whose aromatic character is much more important.

In the case of methyl derivatives of BT or BTO_2 there is a decrease in the rate of the hydrogenation step depending upon the position of the methyl group with a difference between the two series for the methyl in the 2 or 3 position.

BT > 2-MeBT > 3-MeBT > 2,3-diMeBT
BTO_2 > 3-MeBTO_2 > 2-MeBTO_2 > 2,3-diMeBTO_2

If we compare these effects with those obtained in other hydrogenation reactions such as with olefins in cyclohexane series (*30, 31*) where the behavior is steric in origin, we see a marked difference (Table 6).

In our case, it is possible that the effect is not due to a steric origin but instead to an electronic effect.

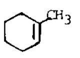
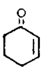
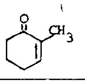
We attempted to test this hypothesis by looking for a correlation between the reactivity of these molecules and their HOMO: the electronic effects give rise to a polarization of the electrons of the molecular orbitals. For this purpose, we determined the vertical ionization potentials of the sulfides and sulfones (*32*) which are reported in Table 7.

According to Koopmans' theorem (*33*), the eigenvalues of the molecular orbitals are related to the first ionization potentials whose values correspond perfectly to the contribution of the molecular orbitals on the different atoms of the molecule.

As presented in Fig. 9: log *k* versus ioni-

TABLE 6

Relative Rate Constants

Structure	Hydrodesulfurization	Structure	Hydrogenation	Reference
BT	1		1	(*30*)
2-MeBT	0.4			
3-MeBT	0.2		4.10^{-2}	(*30*)
2,3-diMeBT	0.1			
BTO_2	1		1	(*31*)
2-MeBTO_2	0.8			
3-MeBTO_2	0.9			
2,3-diMeBTO_2	0.3		5.10^{-2}	(*31*)

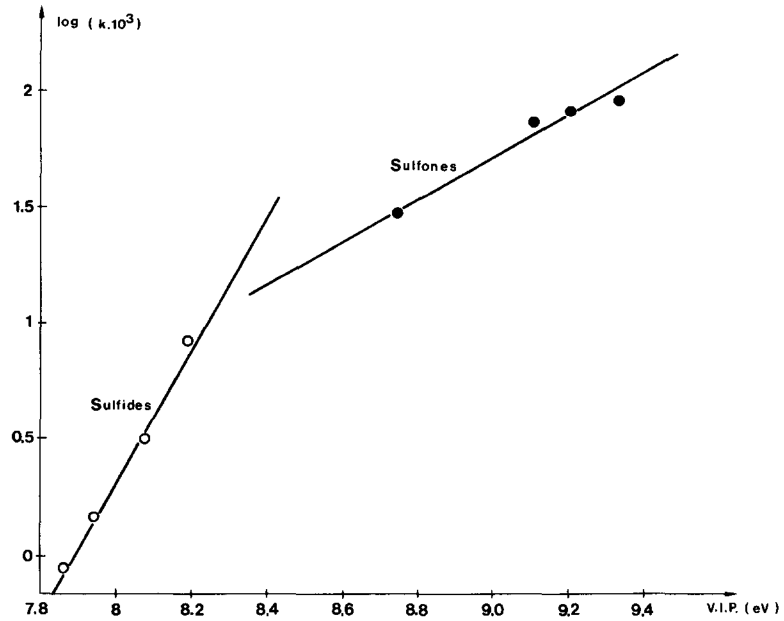


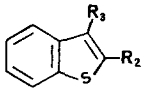
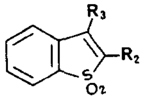
FIG. 9. Logarithm of the rate constant of the first step of the hydrodesulfurization of the sulfides and the sulfones versus vertical ionization potential.

zation potential gives a linear relationship. This correlation shows the influence of electronic effects and that the sulfides are more sensitive than the sulfones. The greater sensitivity of the sulfides (slope = 3) compared to the sulfones (slope = 0.9) is probably due to the more aromatic character of the double bond C_{2-3} in the benzothiophene series.

With this idea in mind, we plan to investigate the influence of other substituents on the reactivity of these molecules.

TABLE 7

Rate Constants of the First Step of the Hydrodesulfurization of the Sulfides and the Sulfones and Vertical Ionization Potentials

	R_2	R_3	No.	10^3k (min^{-1})	Vertical ionization potential (eV)
	H	H	1a	8.4	8.19
	CH_3	H	2a	3.1	8.08
	H	CH_3	3a	1.5	7.95
	CH_3	CH_3	4a	0.9	7.87
	H	H	7a	92	9.32
	CH_3	H	8a	73	9.10
	H	CH_3	9a	81	9.20
	CH_3	CH_3	10a	29	8.74

ACKNOWLEDGMENTS

We owe our gratitude to C.N.R.S. (A.T.P. 77 2379) and to the ELF ERAP Company for financial assistance.

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