JOURNAL OF CATALYSIS 83, 79–84 (1983)

Hydrotreating of Halogeno-Benzo[*b*]Thiophenes and Their *S*-Oxide and *S*-Dioxide Derivatives over CoO–MoO_3/Al_2O_3 Catalyst

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Received November 4, 1982; revised March 10, 1983

Hydrotreating experiments were carried out with a sulfided CoO–MoO_3/Al_2O_3 catalyst at various pressures and temperatures under stirred batch reactor conditions. The reactants were hydrogen and pure halogeno-sulfur compounds in the benzothiophene series. In the case of the benzo[*b*]thiophene itself, the dehalogenation reaction takes place without any observed hydrogenation or hydrodesulfurization. For the *S*-oxidized derivatives a deoxygenation takes place first. For the halogeno-sulfone the dehalogenation is also the first step of the overall process. In the halogeno-benzo[*b*]thiophene series a correlation between the rate constants and the ionisation potential of the molecules suggests that electronic effects may be preponderant.

INTRODUCTION

In the course of our studies on hydrodesulfurization in the benzo[*b*]thiophene and dibenzothiophene series on sulfided CoO–MoO_3/Al_2O_3 catalyst it was possible to show that there was a competition between hydrogenation, desulfurization, or deoxygenation depending upon the molecular model used (*1*, *2*). For example, in the case of sulfoxide derivatives the first step of the entire pathway was deoxygenation prior to any hydrogenation or desulfurization step (*3*) and with dibenzothiophene (*1*) the first step was desulfurization prior to any hydrogenation, whereas for benzo[*b*]naphthothiophene the first step was hydrogenation prior to any desulfurization (*2*). These results are perfectly in accordance with the hypothesis of an anionic vacancy (*4*) at the catalytic site and with the sensitivity of the reaction to electronic effects (*1*, *2*). Due to their strong electronic characteristics we have now tested halogeno derivatives in the sulfide, sulfoxide or sulfone series in order to check the role played by the electronic effects and to try to define more precisely the versatile role played by the Co–Mo hydrotreating catalyst.

EXPERIMENTAL

Catalyst.

The catalyst was Procatalyst HR 306, a desulfurization catalyst used industrially, which has the following composition (wt %) CoO 3 wt%; MoO_3 14 wt%; Al_2O_3 83 wt%. This catalyst was sulfurized using a fluidized bed technique with a gas mixture composed of 3% H_2S and 97% H_2 by volume. The operational pressure was 1 atm, the rate of gas flow was 100 liters/h per 80 g of catalyst and the initial temperature was 150°C. It was increased from 150 to 320°C and held for 2 h at this temperature, then increased to 350°C and held for 2 h at 350°C.

Desulfurization Unit.

The apparatus used for the kinetic studies was an autoclave (Autoclave Engineers, type Magne-drive) with a capacity of 0.3 liter and a system of sampling of liquid during the course of the reaction without stopping the agitation.

Operation

The catalyst, the sulfur compound, and the solvent (dodecane) were placed directly in the autoclave. Air was removed by purging with nitrogen at 6 atm pressure. The

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0021-9517/83 $3.00

temperature was increased at this pressure to 250°C. Hydrogen was introduced at time zero at the desired pressure of 50 atm. Throughout the experiments the sulfur content of the reactant was kept at 0.3% of the weight of the charge.

Reactants and Analysis

1. Benzo[*b*]thiophene was Fluka product whose purity was verified by gas chromatography; mp 30–32°C.

2. The 2,3-dihydrobenzo[*b*]thiophene was prepared by hydrogenation of the corresponding sulfone on a 10% Pd/C catalyst in ethyl alcohol to obtain the dihydrogenated sulfones which, when treated with lithium–aluminum hydride in ether, give the 2,3-dihydrogenated sulfide (5); bp 94–96°C/5 Torr.

3. The halogenobenzo[*b*]thiophenes have been obtained by direct halogenation of benzo[*b*]thiophene in chloroform or carbon tetrachloride. Details are as follows:

3-Bromobenzo[*b*]thiophene bp 92–94°C/0.6 Torr (lit. bp 95°C/1.5 Torr (*6*)).

3-Chlorobenzo[*b*]thiophene and 2,3-dichlorobenzo[*b*]thiophene were obtained by action of chlorine in CCl_4 on benzothiophene (*7*); bp 96–101°C/5 Torr and mp 56–57°C, respectively.

2,3-Dibromobenzo[*b*]thiophene was prepared by addition of bromine in chloroform to benzothiophene (mp 53–55°C).

2-Bromobenzo[*b*]thiophene was obtained by the action of bromine on 2-lithiobenzothiophene which was prepared by the action of n-butyl-lithium on benzothiophene (*8*); mp 44°C.

4. The sulfoxides were obtained by oxidation of the corresponding sulfides with *m*-chloroperbenzoic acid in chloroform at 0°C (*9*). The reaction products were separated by chromatography on silica. 3-Bromobenzo[*b*]thiophene-*S*-oxide, mp 139–141°C (*9*); 2,3-Dichlorobenzo[*b*]thiophene-*S*-oxide, mp 96–98°C (*9*).

5. 3-Bromobenzo[*b*]thiophene-*S*,*S*-dioxide was prepared by oxidation of the 3-bromobenzo[*b*]thiophene with hydrogen peroxide in acetic acid (*10*); mp 183°C.

The products were analyzed by gas chromatography in a Girdel Series 30 flame ionization instrument equipped with an OV 17 column (3%, 3 m, ¼ in.). The following separation conditions were used: injector 300°C, detector 300°C, temperature programming from 70 to 240°C at 5°C/min. The carrier gas was nitrogen at 30 ml/min.

For the halobenzo[*b*]thiophene sulfoxides the analysis was carried out by HPLC on a Waters 6000A instrument with uv detector at 260 nm; the column was a Bondapak CN Waters type and the eluant was a dichloromethane–isopropanol (80/20 v/v)/cyclohexane mixture (5/95).

Kinetic Analysis and Calculations

The reaction orders were determined from experimental results by curve fitting and simulation using a HP 9820A computer equipped with a 9826A tracing table. (For the kinetic consecutive scheme with an order 1 for the starting material the calculation process was described elsewhere (*1*).)

In the case of dihalogenobenzo[*b*]thiophenes the following scheme was used:

$$\begin{tikzcd}
A \arrow[r, "k_1"] \arrow[d, "k_2"'] & B \arrow[d, "k_4"] & & \\
C \arrow[r, "k_3"] & D \arrow[r, "k_5"] & E \arrow[r, "k_6"] & F
\end{tikzcd}$$

where A is the 2,3-dihalogeno-benzo[*b*]thiophene; B, 3-halogeno-benzo[*b*]thiophene; C, 2-halogeno-benzo[*b*]thiophene; D, benzo[*b*]thiophene; E, 2,3-dihydrobenzo[*b*]thiophene; and F ethylbenzene.

It is possible to obtain the individual rate constants by resolving the system of equations:

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

$$(B) = \frac{k_1(A_0)}{k_4 - k}\left[e^{-kt} - e^{-k_4 t}\right]$$

$$(C) = \frac{k_2(A_0)}{k_3 - k}[e^{-kt} - e^{-k_3t}]$$

$$(D) = (A_0)\left[M\frac{e^{-kt}}{k_5 - k} - N\frac{e^{-k_3t}}{k_3 - k} - P\frac{e^{-k_4t}}{k_4 - k} + Qe^{-k_5t}\right]$$

with

$$M = \frac{k_1k_4}{k_4 - k} + \frac{k_2k_3}{k_3 - k}$$

$$N = \frac{k_2k_3}{k_5 - k_3}$$

$$P = \frac{k_1k_4}{k_5 - k_4}$$

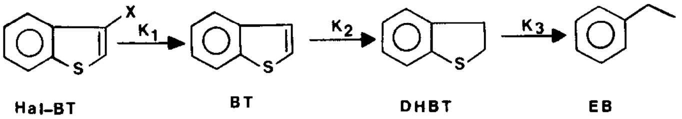
$$Q = \frac{k_1k_4}{(k_5 - k_4)(k_4 - k)} - \frac{k_1k_4}{(k_4 - k)(k_5 - k)} - \frac{k_2k_3}{(k_3 - k)(k_5 - k)} + \frac{k_2k_3}{(k_5 - k_3)(k_3 - k)}$$

where $k = k_1 + k_2$. 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), (D), each at time t, and an approximate value of the rate constants given by curve fitting (and simulation); this treatment has been used for Figs. 1 and 2. The experimental values are the mean of at least three independent runs.

RESULTS

(*1*) *Monohalogeno-benzo*[*b*]*thiophene*

In the case of monohalogeno-benzo[*b*]thiophene (BT) halogenated in the 2- or 3-position (i.e., 2-Br-BT, 3-Br-BT, 3-Cl-BT) the reaction at 250°C and 50 atm gives benzo[*b*]thiophene (BT), dihydrobenzo[*b*]thiophene (DHBT), and ethylbenzene (EB) according to the following consecutive scheme:



The experimental results (concentration versus time as indicated in Fig. 1 for the 3-Br-BT) have been studied by curve fitting and are satisfactorily accounted by a first-order reaction. The rate constants k_1 of the first step are presented in Table 1.

(*2*) *Dihalogeno-benzo*[*b*]*thiophene*

For the dihalogeno compounds 2,3-dibromobenzo[*b*]thiophene (2,3-Br-BT) and 2,3-dichlorobenzo[*b*]thiophene (2,3-Cl-BT) there is a competition between the two hal-

TABLE 1

Rate Constants of the Dehalogenation Reaction of the Monohalogeno-Benzo[*b*]thiophene Derivatives

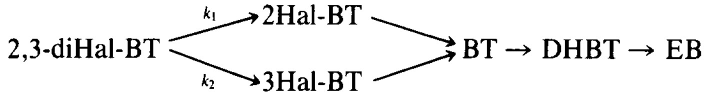
Compound	$k_1 \times 10^3$ min^{-1}(g cat)$^{-1}$
2-Br-BT	128 ± 10
3-Br-BT	108 ± 6
3-Cl-BT	30 ± 4

TABLE 2

Rate Constants of the Dehalogenation Reaction of the Dihalogeno-Benzo(*b*)thiophene Derivatives

Compound	$k_1 \times 10^3$ min^{-1} (g cat)$^{-1}$	$k_2 \times 10^3$ min^{-1} (g cat)$^{-1}$
2,3-diCl-BT	37 ± 2	1 ± 0.05
2,3-diBr-BT	165 ± 10	28 ± 3

ogen atoms located in the 2- or 3-position. The experimental results (concentration versus time as indicated in Fig. 2 for the 2,3-Cl-BT) are in good agreement with the following kinetic scheme:



$$\begin{tikzcd}[row sep=small] & \text{2Hal-BT} \arrow[dr] & & & \\ \text{2,3-diHal-BT} \arrow[ur, "k_1"] \arrow[dr, "k_2"'] & & \text{BT} \arrow[r] & \text{DHBT} \arrow[r] & \text{EB} \\ & \text{3Hal-BT} \arrow[ur] & & & \end{tikzcd}$$

The rate constants of the two competitive steps are presented in Table 2.

(*3*) *Sulfoxides*

For the sulfoxides, 3-bromobenzo[*b*]thiophene-*S*-oxide and 2,3-dichlorobenzo[*b*]thiophene-*S*-oxide, the conditions of the reaction are those defined previously, namely 70°C and 10 atm, because in that case, as in the methyl series (*1*), the first reaction is the deoxygenation prior to any other one leading to the corresponding halobenzo[*b*]thiophene (*3*).

(*4*) *Sulfones*

For the sulfones the problem is more complicated due to the easy decomposition of the reactant (*11*, *12*). However, for the 3-Br-BT sulfone it was possible to show that at 190°C and 50 atm (with a sulfur content at 0.043% of the weight of the charge) the first step was debromination to give the sulfone

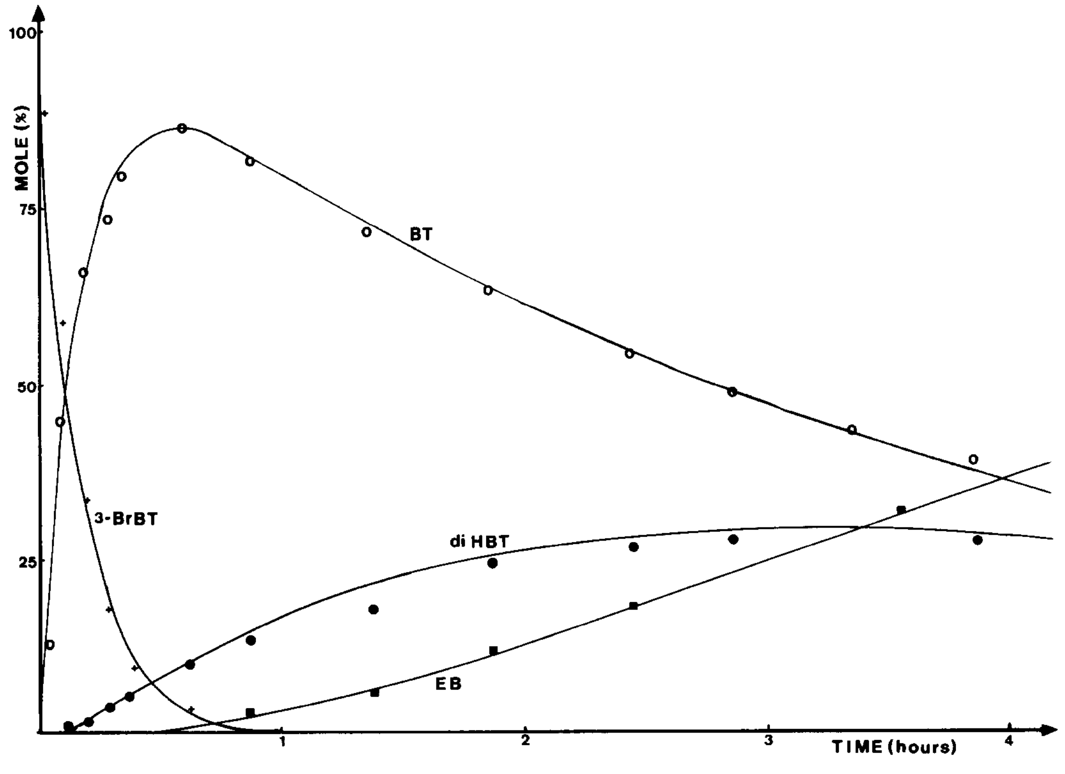


FIG. 1. Desulfurization of 3-bromobenzo[*b*]thiophene (3-Br-BT) (T = 250°C; p_{H_2} = 50 atm; wt% of S based on charge = 0.3).

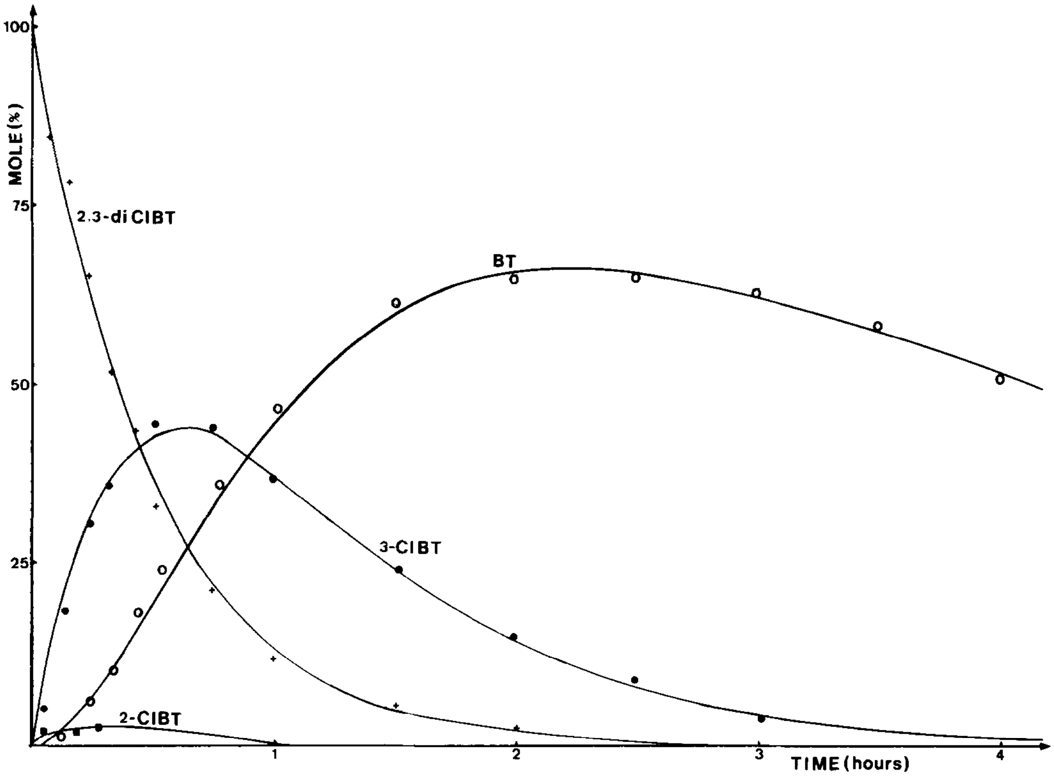


FIG. 2. Desulfurization of 2,3-dichlorobenzo[*b*]thiophene (2,3-Cl-BT) (T = 250°C; p_{H_2} = 50 atm; wt% of S based on charge = 0.3).

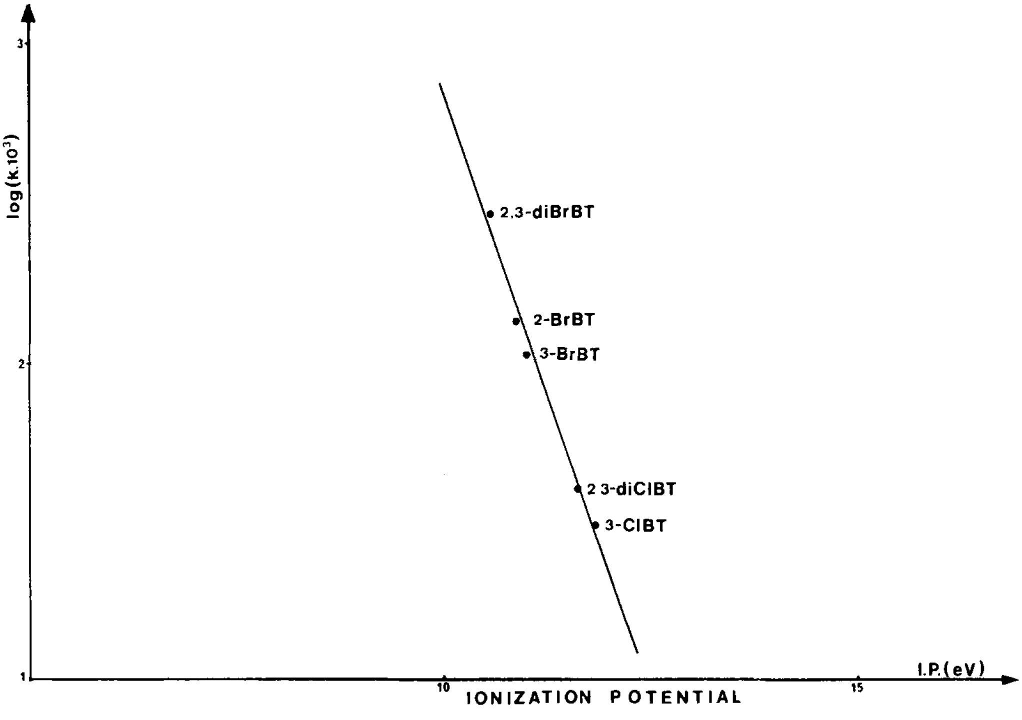


FIG. 3. Logarithm of the rate constant of the first step of the hydrodehalogenation process of the sulfides versus ionization potentials of the π lone electron pairs of the halogen atoms.

itself. In a competitive reaction between equal amounts of 3-Br-BT sulfone and 3-Br-BT the rate of debromination for the sulfone was 10 times faster than the corresponding sulfide.

DISCUSSION

Different effects can be presented through the comparison of the results obtained from the halogeno 2- and 3-benzo[*b*]thiophenes and their homologs sulfoxide or sulfone.

As shown, halogeno-benzo[*b*]thiophene and their sulfones have the same behavior with a dehalogenation reaction as the first step through a consecutive kinetic scheme with an order of one for the reactants. For the sulfoxides the first step is a deoxygenation, as previously shown for the methyl derivatives (*3*). The experimental conditions allow us to obtain very easily the corresponding halogeno-benzo[*b*]thiophene. The kinetic scheme is still a consecutive one but the order in reactant is zero probably due to a different adsorption process.

From the rate constants of the halogeno benzo[*b*]thiophene the order of reactivity is the following 2,3-Br-BT > 2-Br-BT ~ 3-Br-BT > 2,3-ClBT > 3-ClBT. According to the nature of the halogen atom Cl or Br, the C–Br bond is more easily hydrogenolyzed than the C–Cl bond (3 to 5 times) and the rate of the dehalogenation for the halogen in the 2- or 3-position is almost identical.

As in the case of the benzo[*b*]thiophene methyl derivatives (*1*), we attempted to test the influence of the electronic effect on the reactivity by looking for a correlation between the rate constants and the HOMO of the molecules since the electronic effects give rise to a polarization of the electrons of the molecular orbitals. For this purpose the ionization potentials were determined (*13*). Plotting log $k_{\text{dehalogenation}}$ versus the ionization potentials corresponding to the π electron pairs of the halogen atoms, a good linear correlation is obtained (correlation coefficient 0.99) as shown in Fig. 3. These results are evidence for the important role played by electronic effects and are in accordance with the hypothesis of an anionic vacancy at the catalytic site (*4*).

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