

# Transformation of thiophenic compounds over HY zeolite Study of the acid-catalyzed isomerization and disproportionation mechanisms by quantum chemical calculations

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## Abstract

The transformation of thiophenic compounds (2-methylthiophene, 3-methylthiophene, 2-methylbenzothiophene and 3-methylbenzothiophene) was carried out in a fixed bed reactor at 350 °C under atmospheric pressure in the presence of a HY zeolite with a Si/Al ratio equal to 16. All the reactants underwent both isomerization and disproportionation. The product selectivities obtained experimentally were rationalized on the basis of the calculated stabilities (B3LYP method) of the expected cationic intermediates. These calculations allowed to explain why 2-methylthiophene and 3-methylthiophene presented the same reactivity in isomerization and why the methylbenzothiophene isomers were more reactive than the methylthiophene isomers. Moreover, the distribution of the dimethylthiophenes and dimethylbenzothiophenes obtained by disproportionation of the methylthiophene and methylbenzothiophene isomers, respectively, was in good agreement with the relative stabilities of the carbenium ions involved in these reactions.

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## 1. Introduction

Thiophenic and benzothiophenic compounds are major impurities in the gasoline originating from FCC naphtha [1–3]. In Western Europe, the FCC naphtha represents about 27 vol.% of the commercial gasoline [4]. Since the maximum sulfur content allowed in fuels is 50 ppm by now and will be 10 ppm or less by 2009 [5], the deep desulfurization of gasoline is receiving increasing attention. For example, a possible approach is to increase the boiling point of the sulfur impurities through alkylation with the olefins present in the gasoline. This makes it possible to shift the sulfur compounds from light to heavier fractions of the gasoline. Therefore, these alkylated compounds can be eliminated by distillation. British Petroleum developed this process under the name OATS® (Olefinic Alkylation of Thiophenic Sulfur) [6,7]. The alkylation of 3-methylthiophene

with 2-methylbut-2-ene was studied in a batch reactor at 85 °C over HY zeolites [8] and over supported phosphoric acid [9]. Another possibility is to transform these compounds through disproportionation. In a previous study [10], the transformation of thiophenic compounds was carried out over HY, H $\beta$ , HZSM5 and H-mordenite zeolites at 350 °C under atmospheric pressure. Two main reactions were observed: isomerization and disproportionation. The HY zeolite with a Si/Al atomic ratio of 16 was found to be the most selective in disproportionation.

The isomerization and disproportionation mechanisms were investigated using the Density Functional Theory (DFT) method [11–17]. For the isomerization of toluene on acidic mordenite using the periodic density theory Vienna ab initio simulation package (VASP) [18,19], it was shown that the intramolecular isomerization was easier than the intermolecular isomerization [11,12]. When a small zeolite cluster model was used, it was also shown that the 1,2-methyl shift mechanism was expected to be more favoured than the bimolecular mechanism for methylthiophene isomerization [13]. Furthermore, the isomerization of sulfur compounds such as 4,6-dimethyldibenzothiophene

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occurred only through an intramolecular methyl shift [14]. The disproportionation mechanism of xylene over mordenite was also investigated using the VASP method [15]. The proposed mechanism involved the formation of a bimolecular carbocation which led to a trimethyldiphenylmethane intermediate. A quantum mechanical-molecular mechanical (QM/MM) method [20] was also used for the investigation of the disproportionation mechanism of *m*-xylene [16,17].

The aim of the present contribution was to investigate the mechanisms of the acid-catalyzed isomerization and disproportionation of the methylthiophene and methylbenzothiophene isomers, whatever the nature of the catalyst. For this purpose, the stabilities of the carbenium ions involved in these mechanisms were calculated by using the B3LYP method [21] without taking into consideration the zeolite framework.

## 2. Experimental

### 2.1. Materials

2-Methylthiophene (2-MT, 98%), 3-methylthiophene (3-MT, 98%) and 2-methylbenzothiophene (2-MBT, 97%) were purchased from Aldrich; 3-methylbenzothiophene (3-MBT, 95%) from Lancaster and cyclohexane from SDS. The position numbering in the structural formulas of these sulfur compounds is presented in Table 1.

The unit cell formula of the commercial dealuminated HY-zeolite (CBV720, supplied by Conteka) used in this study was  $\text{Na}_{0.3}\text{H}_{11}\text{Al}_{11.3}\text{Si}_{180.7}\text{O}_{384}$ . The composition of the zeolite was determined by chemical analysis (CNRS, Service Central d'Analyses, 69390 Vernaison, France). The BET surface area (nitrogen adsorption measured at  $P/P_0 = 0.100$  by using an automatic Micromeritics ASAP 2010 apparatus) was  $847\text{ m}^2\text{ g}^{-1}$ . The micropore volume determined by the t-plot method was  $0.298\text{ cm}^3\text{ g}^{-1}$ . The acidity of this zeolite was measured by IR spectroscopy of adsorbed pyridine (Nicolet Magna IR 550 Fourier transform spectrometer). The concentrations of the Brønsted ( $0.247\text{ mmol g}^{-1}$ ) and Lewis ( $0.076\text{ mmol g}^{-1}$ ) sites able to retain pyridine at  $150^\circ\text{C}$  were determined by using the areas of the bands at  $1545$  and  $1450\text{ cm}^{-1}$  with the extinction coefficients of  $1.13$  and  $1.28\text{ cm}^2/\mu\text{mol}$ , respectively [22].

### 2.2. Procedure

The transformation of the thiophenic compounds was carried out in a fixed bed reactor made of Pyrex glass at  $350^\circ\text{C}$  under atmospheric pressure. The liquid mixture was introduced in the reactor by a syringe pump. The partial pressure of cyclohex-

ane which was used to dilute the reactants was  $18.9\text{ kPa}$ . The partial pressures of the reactants (methylthiophenes or methylbenzothiophenes) were  $1.7\text{ kPa}$ . The partial pressure of  $\text{N}_2$  used as carrier gas was  $80.7\text{ kPa}$ . The particle size of the catalyst was in the range of  $250\text{--}315\text{ }\mu\text{m}$ . The weight of the catalyst samples varied between  $0.025$  and  $0.200\text{ g}$ . Before each experiment, the catalyst was activated at  $500^\circ\text{C}$  in a flow of air for  $12\text{ h}$ . The contact time of the reactant ( $t_c$ ) was varied between  $3$  and  $57\text{ s}$ . It was deduced from the formula:

$$t_c = \frac{V_c}{D}(\text{s})$$

where  $V_c$  is the catalyst volume ( $\text{cm}^3$ ) and  $D$  is the gas flow rate of the thiophenic compound ( $\text{cm}^3/\text{s}$ ).

### 2.3. Chromatographic analysis

The samples were analysed with a Varian 3400 chromatograph. For the 2-MT and 3-MT reactants, the column was a DB5 capillary column (length:  $30\text{ m}$ ; diameter:  $0.32\text{ mm}$ ; film thickness:  $0.25\text{ }\mu\text{m}$ ). For the 2-MBT and 3-MBT reactants, the column was a CPWAX capillary column (length:  $30\text{ m}$ ; diameter:  $0.25\text{ mm}$ ; film thickness:  $0.50\text{ }\mu\text{m}$ ). The products were identified by adding aliquots of commercial compounds to the reaction samples, by using GC/MS analysis (Finnigan INCOS 500) and by comparison of the chromatograms with literature data [23–25].

## 3. Computational details

The zeolite framework was not taken into account in the computation. The calculations were performed on gas-phase systems using the B3LYP density functional method [21] with the split valence plus polarization 6-31G(d,p) basis set. All structures were fully optimized and a vibrational analysis was performed to characterize each stationary point as a minimum or a transition state structure (zero or one imaginary vibrational frequency). Small effects like thermal and zero point energy corrections were neglected. In addition, when comparisons with the experimental results were possible, more accurate calculations were performed using the composite G3MP2 method [26]. The calculations were carried out with the *Gaussian 03* package [27].

## 4. Results and discussion

### 4.1. Isomerization pathway

#### 4.1.1. Isomerization activity of the HY zeolite

2-MT and 3-MT transformed into each other through isomerization. This was also the case for 2-MBT and 3-MBT. The isomerization reactions were not very sensitive to HY deactivation. The isomerization activities for the transformation of the thiophenic compounds (2-MT, 3-MT, 2-MBT and 3-MBT) were determined for conversions lower than  $10\text{ mol}\%$ . Table 2 shows that 2-MT and 3-MT had about the same reactivity in isomerization, while 3-MBT was only  $1.3$  times more reactive than 2-MBT. Moreover, the methylbenzothiophene isomers

Table 1  
Position numbering in sulfur compounds


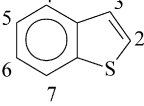
	
thiophenic compound	benzothiophenic compound

Table 2  
Transformation of 2-MT, 3-MT, 2-MBT and 3-MBT at 350 °C under atmospheric pressure

Thiophenic compounds	Isomerization activity (mmol/h g)	Disproportionation activity (mmol/h g)
2-MT	0.20	0.23
3-MT	0.20	0.14
2-MBT	2.18	0.95
3-MBT	2.82	0.95

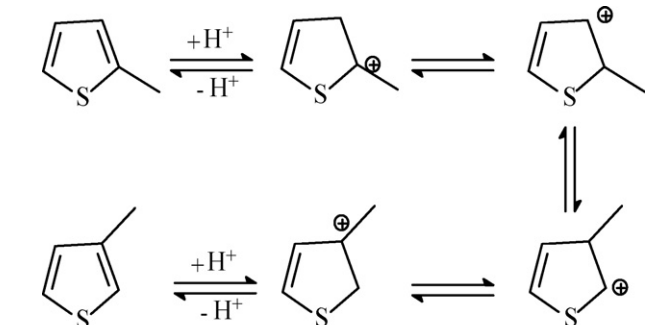
Activity of the stabilized HY zeolite [10].

were more reactive in isomerization than the methylthiophene isomers. For example, 3-MBT was about 14 times more reactive than 3-MT (Table 2).

#### 4.1.2. Calculations of the stabilities of the carbenium ions involved in the isomerization mechanism

Two mechanisms allow to explain the isomerization reactions: one, intramolecular involving 1,2-methyl shift; the other, intermolecular involving transalkylation. With aromatic hydrocarbons such as xylene, the contribution of the intermolecular mechanism is always of minor importance compared to the intramolecular mechanism [28–31]. This is also the case for thiophenic compounds [10]. This mechanism involves the initial protonation of the thiophenic compound which leads to a carbenium ion in which the isomerization step takes place through hydride and methyl shifts (Scheme 1).

Though the zeolite framework was not taken into account in our calculations, some aspects of the isomerization mechanism can be clarified. We examined the hydride shift and methyl shift involved in the intramolecular isomerization mechanism. The results of these calculations are reported in Figs. 1 and 2 for MT and MBT systems, respectively. The carbenium ions obtained initially from the protonation of the isomers alkylated in position 3 are more stable than those obtained from the protonation of the isomers alkylated in position 2. These results can be explained by the more favourable position of the cationic charge with respect to the double bond (MT isomer) or aromatic ring (MBT isomer). As expected, the methyl shift is the rate-limiting step, in accordance with the results obtained by Rozanska et al. [13]. Indeed, the activation energy barrier that is required to achieve the methyl shift is 155 kJ mol<sup>-1</sup> starting from the 3-MT carbenium ion (Fig. 1) and 141 kJ mol<sup>-1</sup> starting from the 3-



Scheme 1. Isomerization of 2-MT and 3-MT into each other through hydride and methyl shift [10].

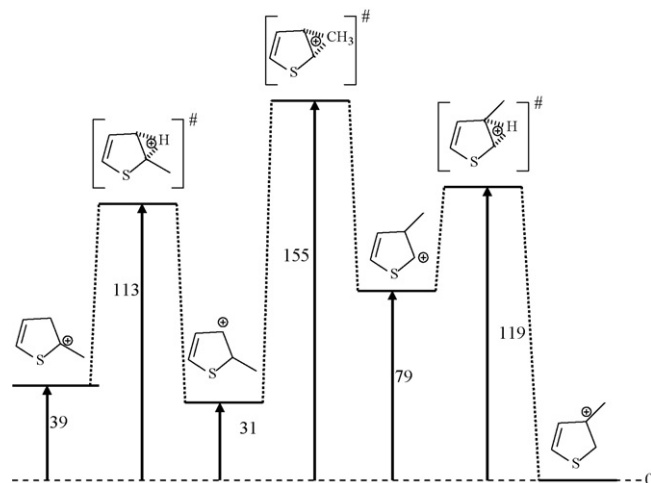


Fig. 1. Reaction energy diagram of the intermediates and transition states for the isomerization mechanism of 2-MT and 3-MT (data in kJ mol<sup>-1</sup>).

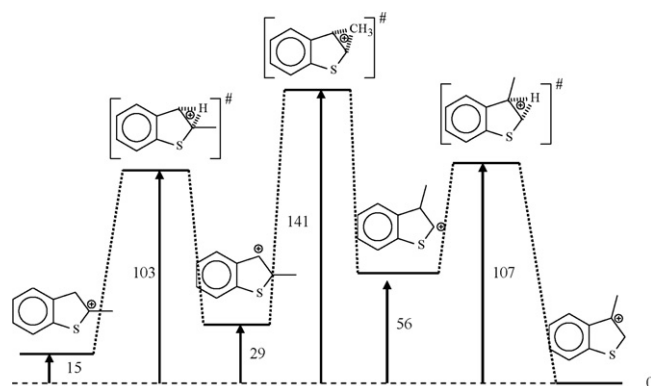


Fig. 2. Reaction energy diagram of the intermediates and transition states for the isomerization mechanism of 2-MBT and 3-MBT (data in kJ mol<sup>-1</sup>).

MBT carbenium ion (Fig. 2). These calculations can explain why 3-MBT was more reactive than 3-MT in isomerization (Table 2).

We calculated the relative stabilities of the 2-MT and 3-MT isomers. At the B3LYP/6-31G(d,p) level, both isomers are very close in energy (Table 3). To improve this analysis, the relative stabilities of these two isomers were determined by calculating the free energies at 350 °C at the higher accuracy G3MP2 level. These calculations confirmed the B3LYP results since 2-MT was found to be more stable than 3-MT by only 0.4 kJ mol<sup>-1</sup> (Table 3). As the methyl shift is the rate-limiting step which is the same for both isomers (2-MT and 3-MT), their reactiv-

Table 3  
Relative stabilities calculated by the B3LYP/6-31G(d,p) method and relative G3MP2 free energies at 350 °C of the methylthiophene and methylbenzothiophene isomers (in kJ mol<sup>-1</sup>)

	Relative energy obtained by the B3LYP method	Relative free energy obtained by the G3MP2 method
2-MT	0.0	0.0
3-MT	0.0	0.4
2-MBT	0.0	0.0
3-MBT	1.3	1.1

ities should depend on their stabilities. It is the case since we observed that 2-MT and 3-MT had about the same reactivity in isomerization (Table 2).

We also calculated the relative stabilities of the 2-MBT and 3-MBT isomers. At the B3LYP/6-31G(d,p) level, 2-MBT is more stable than 3-MBT (Table 3). If we consider that the reactivities of the MBT isomers in isomerization depend on their stabilities, the barrier height for the 3-MBT isomerization should be  $1.3 \text{ kJ mol}^{-1}$  lower than for the 2-MBT isomerization. We can conclude that 3-MBT is predicted to be slightly more reactive than 2-MBT, which is in agreement with the relative reactivities obtained experimentally (Table 2), in spite of the fact that the zeolite framework was not considered in these calculations. As for the MT isomers, we improved the results by computing the G3MP2 free energies at  $350^\circ\text{C}$ . At this level of calculation, the values of the relative stabilities of 2-MBT and 3-MBT are again close to the B3LYP result (Table 3).

#### 4.2. Disproportionation pathway

##### 4.2.1. Selectivity of the HY zeolite in the disproportionation pathway

Over HY zeolite, disproportionation of 2-MT and 3-MT led to thiophene and dimethylthiophenes which were obtained in about equimolar quantities. 2-MBT and 3-MBT led also to benzothiophene and dimethylbenzothiophenes in about equimolar amounts. 2-MT was more reactive in disproportionation than 3-MT, while 2-MBT and 3-MBT had the same reactivity (Table 2).

Fig. 3 shows that 2-MT led to three primary disproportionation products: 2,3-DMT; 2,4-DMT and 2,5-DMT, in addition to thiophene. 2,5-DMT was the main DMT isomer observed at low conversion of 2-MT. At a higher conversion, its concentration decreased and it gave 2,4-DMT through isomerization. 2,3-DMT was observed in small quantities and its concentration was independent on the conversion of 2-MT. 3,4-DMT was present in trace amounts only.

By disproportionation, 3-MT led also to three primary products: 2,3-DMT; 2,4-DMT and 3,4-DMT (Fig. 4), in addition to thiophene. 2,5-DMT was also observed at high conversion and was probably formed through isomerization of 2,4-DMT.

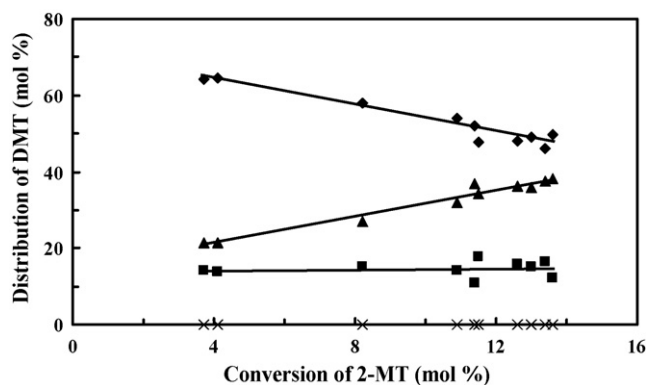


Fig. 3. Transformation of 2-MT over HY zeolite at  $350^\circ\text{C}$  under atmospheric pressure. Effect of the conversion on the distribution of the dimethylthiophene isomers. 2,3-DMT (■); 2,4-DMT (▲); 2,5-DMT (◆); 3,4-DMT (×).

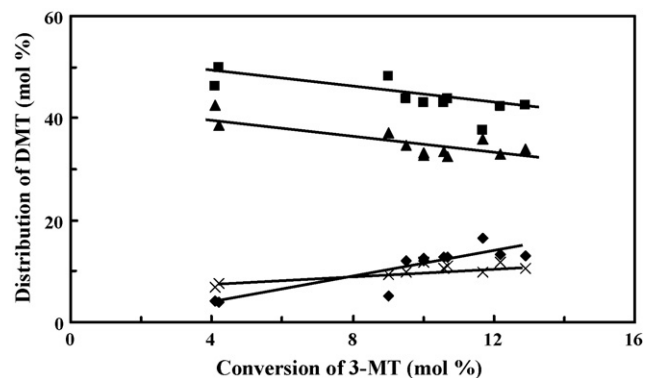


Fig. 4. Transformation of 3-MT over HY zeolite at  $350^\circ\text{C}$  under atmospheric pressure. Effect of the conversion on the distribution of the dimethylthiophene isomers. 2,3-DMT (■); 2,4-DMT (▲); 2,5-DMT (◆); 3,4-DMT (×).

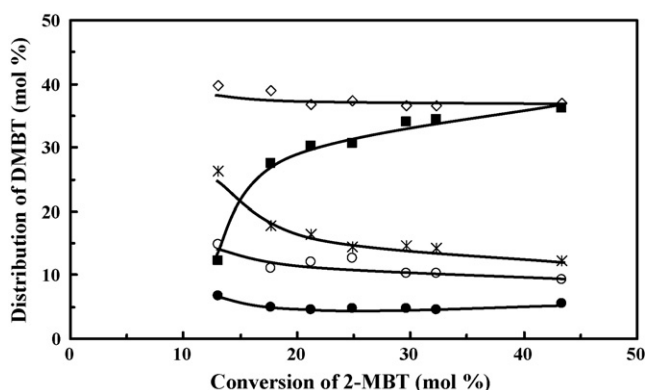


Fig. 5. Transformation of 2-MBT over HY zeolite at  $350^\circ\text{C}$  under atmospheric pressure. Effect of the conversion on the distribution of the dimethylbenzothiophene isomers. 2,3-DMBT (◇); 2,4-DMBT (●); 2,5-DMBT (○); 2,6-DMBT (✱); other DMBT (■).

Both 2-MBT (Fig. 5) and 3-MBT (Fig. 6) led to 2,3-DMBT as the major DMBT product obtained by disproportionation, but other isomers were also formed.

2-MBT led to four primary DMBT products: 2,3-DMBT; 2,4-DMBT; 2,5-DMBT and 2,6-DMBT, in addition to benzothiophene. Their concentrations followed the sequence

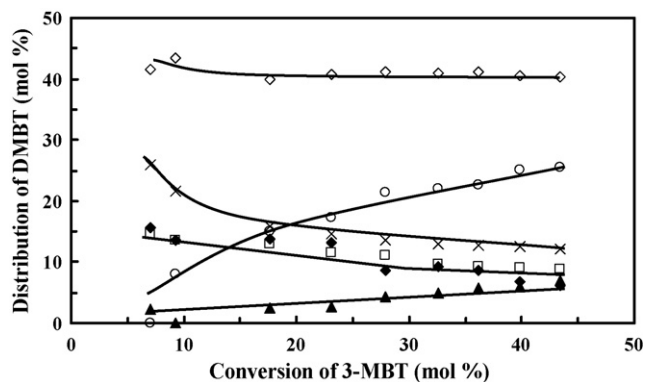
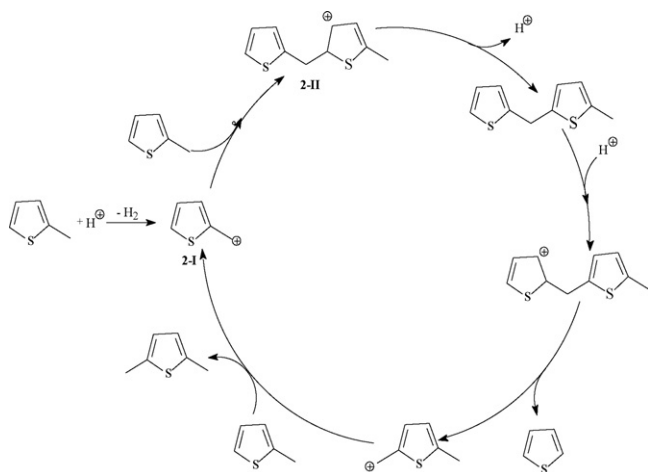


Fig. 6. Transformation of 3-MBT over HY zeolite at  $350^\circ\text{C}$  under atmospheric pressure. Effect of the conversion on the distribution of the dimethylbenzothiophene isomers. 2,3-DMBT (◇); 3,4-DMBT (◆); 3,5-DMBT (□); 3,6-DMBT (×); 3,7-DMBT (▲); other DMBT (○).



Scheme 2. Acid-catalyzed disproportionation mechanism of 2-MT leading to thiophene and 2,5-DMT [10].

2,3-DMBT > 2,6-DMBT > 2,5-DMBT > 2,4-DMBT (Fig. 5). Four other isomers were also obtained: 3,4-DMBT; 3,5-DMBT; 3,6-DMBT and 3,7-DMBT. These isomers were secondary products and were formed through isomerization by methyl shift of the isomers alkylated in position 2.

The concentrations of the DMBT isomers obtained at low conversion by disproportionation of 3-MBT followed the sequence: 2,3-DMBT > 3,6-DMBT > 3,5-DMBT = 3,4-DMBT > 3,7-DMBT (Fig. 6). Other isomers (2,4-DMBT; 2,5-DMBT and 2,6-DMBT) formed through the isomerization of the primary products with a methyl group in position 3 were also observed as secondary products.

#### 4.2.2. Calculations of the stabilities of the carbenium ions involved in the disproportionation mechanism

The disproportionation mechanism of 2-MT leading to thiophene and 2,5-DMT was reported previously [10]; it is shown in Scheme 2. This mechanism is in accordance with the proposals made for toluene and xylene disproportionation [15–17,31–35].

Table 5

Calculated relative energies of the dimethylthiophenes by the B3LYP method (in  $\text{kJ mol}^{-1}$ )

	Relative energy
2,3-DMT	4.9
2,4-DMT	0.0
2,5-DMT	0.2
3,4-DMT	0.3

In the initial step, adsorbed 2-MT reacts with a proton and loses a methyl hydrogen to form  $\text{H}_2$  and a 2-thienylcarbenium ion (2-I) which can react with another 2-MT molecule. An intermediate bimolecular carbenium ion (2-II) is obtained. After deprotonation and protonation on the second thiophenic ring, a bond scission can occur and thiophene is formed together with a carbenium ion corresponding to 2,5-DMT. This carbenium ion may then abstract a hydride from another 2-MT molecule and desorb, leading to 2,5-DMT.

The difference in the distributions of the dimethylthiophene and dimethylbenzothiophene isomers resulting, respectively, from the disproportionation of methylthiophenes and methylbenzothiophenes can be explained by the stabilities of the carbenium ions of type 2-II.

Table 4 clearly shows that the carbenium ion 2-II, leading to 2,5-DMT, is the most stable of all the carbenium ions involved in the disproportionation mechanism. These results are in good agreement with the fact that the hydrogen in the  $\alpha$ -position to the sulfur atom is favoured in the electrophilic substitution of thiophenes [36]. However, despite the fact that the carbenium ion leading to 2,3-DMT was more stable than the carbenium ion leading to 2,4-DMT (Table 4); 2,3-DMT and 2,4-DMT were formed in about the same quantities at low conversion (4 mol%) (Fig. 3).

Whatever the conversion of 3-MT, the concentrations in dimethylthiophene isomers followed the sequence 2,3-DMT > 2,4-DMT  $\gg$  3,4-DMT, which corresponds to the order

Table 4

Calculated relative energies of carbenium ions involved in the disproportionation of 2-MT and 3-MT (in  $\text{kJ mol}^{-1}$ )<sup>a</sup>

2-MT reactant			3-MT reactant		
DMT product	Intermediate carbenium ion	Relative energy	DMT product	Intermediate carbenium ion	Relative energy
2,3-DMT		44	2,3-DMT		4
2,4-DMT		61	2,4-DMT		18
2,5-DMT		0	3,4-DMT		62

<sup>a</sup> For each of these species, several conformers exist. To save computer time, we considered only one conformer. To select it we performed a conformational analysis at the semi-empirical AM1 level. The resulting lower conformer was then reoptimized by the B3LYP method. The lower conformer at the AM1 level is likely to be the same as the one at the B3LYP level.

Table 6

Calculated relative energies of carbenium ions involved in the disproportionation of 2-MBT and 3-MBT (in  $\text{kJ mol}^{-1}$ )

2-MBT reactant			3-MBT reactant		
DMBT product	Intermediate carbenium ion	Relative energy	DMBT product	Intermediate carbenium ion	Relative energy
2,3-DMBT		12	2,3-DMBT		0
2,4-DMBT		31	3,4-DMBT		50
2,5-DMBT		45	3,5-DMBT		50
2,6-DMBT		29	3,6-DMBT		44
2,7-DMBT		48	3,7-DMBT		54

See footnote in Table 4.

of stability of the type 2-II bimolecular carbenium ions involved in their formation (Table 4). One can notice that this sequence does not correspond to the relative stabilities of the dimethylthiophene isomers (Table 5).

Table 6 shows that the carbenium ions involved in the formation of 2,3-DMBT from both 2-MBT and 3-MBT are more stable than the other carbenium ions. This can explain why 2,3-DMBT which was not favoured by thermodynamics (Table 7), was nevertheless the major product of 2-MBT and 3-MBT disproportionation (Figs. 5 and 6).

Regarding 2-MBT disproportionation, the sequence of the stabilities of the bimolecular carbenium ions calculated by the B3LYP method was 2,3-DMBT > 2,4-DMBT  $\approx$  2,6-DMBT > 2,5-DMBT (Table 6). If we except 2,4-DMBT, this sequence is close to the concentration sequence observed experimentally which was 2,3-DMBT > 2,6-DMBT > 2,5-DMBT > 2,4-DMBT.

Table 7

Calculated relative energies of the dimethylbenzothiophenes by the B3LYP method (in  $\text{kJ mol}^{-1}$ )

	Relative energy
2,3-DMBT	6.1
2,4-DMBT	2.8
2,5-DMBT	3.8
2,6-DMBT	3.5
2,7-DMBT	0
3,4-DMBT	16.4
3,5-DMBT	5.1
3,6-DMBT	5.6
3,7-DMBT	1.2

On the other hand, Table 6 shows that the stabilities of the bimolecular ions involved in the disproportionation of 3-MBT followed the sequence: 2,3-DMBT > 3,6-DMBT > 3,5-DMBT = 3,4-DMBT > 3,7-DMBT, which is in good agreement with the concentrations of the DMBT isomers obtained at low conversion by disproportionation of 3-MBT (Fig. 6).

## 5. Conclusion

When reacted over a HY zeolite at 350 °C, under atmospheric pressure in a fixed bed reactor, the thiophenic compounds used in this study (namely 2-MT, 3-MT, 2-MBT and 3-MBT) led mainly to isomerization and disproportionation reactions.

Isomerization occurred through an acid-catalyzed step by step intramolecular mechanism in which the 1,2-methyl shift was the rate-limiting step as shown by DFT calculations. In fact, 2-MT and 3-MT presented the same reactivity due to the same stability, whereas 3-MBT, which was less stable than 2-MBT, was a little more reactive than the latter in isomerization. In addition, the methyl shift energy barrier, calculated using the B3LYP method, allowed to explain why the methylbenzothiophene isomers were more reactive than the methylthiophene isomers in isomerization.

The disproportionation mechanism occurred through a bimolecular cationic mechanism. By this mechanism, thiophene and dimethylthiophenes were formed from methylthiophene. The distribution of the dimethylthiophene isomers was accounted for on the basis of the stability of the bimolecular carbenium ions formed initially. The same explanation was proposed for the distribution of the dimethylbenzothiophene

isomers obtained by disproportionation of the methylbenzothio-  
iophene isomers.

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