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Electronic effect of substituents on the hydrodesulfurization of ring substituted benzenethiols

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Abstract

To clarify the electronic factors of the reactants affecting hydrodesulfurization (HDS) reactivity, the o-, m- and p-isomers of aminobenzenethiol (ABT), methoxybenzenethiol (MBT) and toluenethiol (TT) were hydrogenolyzed by a batch method over CoS₂, NiS₂ and a presulfided commercial HDS catalyst.

In the hydrogenolysis of all the isomers of ABT, MBT and TT, HDS by cleavage of the C-S bond occurred selectively and was promoted by the presence of electron-releasing substituents in the *ortho*- and *para*-positions.

Among the quantities obtained from the MINDO/3 calculation for a reactant, the next three are especially interesting: these are the coefficients of the *ipso*-carbon and the sulfur atoms in the highest occupied π -orbital (π -HOMO), C^{HOMO}_C and C^{HOMO}_S, and the energy level of π -HOMO.

The differences in reactivity among the isomers of a substituted benzenethiol can be interpreted by use of the frontier π -electron densities (FED), $2(C_{\rm C}^{\rm HOMO})^2$ and $2(C_{\rm S}^{\rm HOMO})^2$. On the other hand, the differences in reactivity among the molecules, *i.e.*, ABT, MBT, TT, and benzenethiol, shows a close correlation with the ratio of the two FEDs, $(C_{\rm C}^{\rm HOMO}/C_{\rm S}^{\rm HOMO})^2$, and also with the energy level of π -HOMO.

It is suggested that the energy level and the FED assume an important role in the HDS reactivities and that the magnitudes of the FEDs on the positions of both the sulfur and the *ipso* carbon atoms affect the reactivities not independently but concertedly.

Key words: electron-releasing substituents; frontier electron density; hydrodesulphurization; promoting effect; substituted benzenethiols

Introduction

Since the content of organic sulfur compounds in petroleum fractions increases with increased boiling point of the fraction [1], elucidation of HDS

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reaction mechanisms is significant not only of the theoretically but also for effective use of heavy feedstocks.

There might be two approaches to the above subject. One is a catalytic approach, and many papers have been published on catalytic activities connected with catalytic compositions, preparative conditions and surface structure. The other is a reactant approach in relation to molecular structure and/ or properties.

In the latter case, thiophene, benzothiophene, dibenzothiophene and their various derivatives have been used as exemplary compounds, and detailed studies have been reported. These studies may be classified as follows:

(1) On the basis of the data on reaction rate or product contributions, the type of the catalytic active site was discussed [2-8].

(2) The structural effects of methyl- or phenyl-substituents on the reaction were studied, and the pathways were discussed in terms of electron resonance and steric crowding [9].

(3) The effects of additives on the reaction were studied, and the kinds of catalytic active sites or adsorption mechanisms were discussed [10-16].

The HDS of phenothiazine, phenoxathiine, thianthrene and thioxanthene has also been studied. These studies may be classified as follows:

(4) From the product contribution, the reaction paths were investigated and compared with each other [17,18].

(5) Using the measured reaction rate constants, the reactivities were compared with those of dibenzothiophene in terms of molecular structure (planar or folded) [19-21].

In recent years, several articles have been published on the hydrogenolysis of substituted benzenes and pyridine derivatives, in which the reactivities were discussed in view of the electronic effects of the substituents [22-25]. However, few studies [26-29] on the relationship between HDS reactivities and the electronic states of the reactants have appeared.

In order to obtain fundamental knowledge on the HDS reactivity of organic sulfur compounds, we have previously studied the hydrogenolysis of substituted benzenethiols over molybdenum(VI) sulfide catalyst [30] and have reached the following conclusions:

(a) The cleavage of the aromatic C-S bond is promoted by the presence of electron-releasing substituents at the *para*- or *ortho*-position.

(b) The extent of the promoting effect is approximately related to the magnitude of the electron-releasing property of the substituents.

(c) The HDS reactivity of heterocyclic sulfur compounds such as phenothiazine and benzothiazole may be interpreted similarly to the concept of the electron-releasing property.

However, it is not clear whether the promoting effect described above is observed as a general phenomenon, that is, not only in the case of molybde-num(VI) sulfide catalyst but also in most of the cases where various HDS catalysts are used. In order to clarify this question, hydrogenolysis of the ring

substituted benzenethiols was investigated over cobalt (IV) sulfide, nickel (IV) sulfide and a presulfided commercial HDS catalyst. The results are discussed in terms of the electronic states of the reactants, which were calculated using a semi-empirical molecular orbital method (MINDO/3).

Experimental

Materials and catalysts

The isomers of aminobenzenethiol, methoxybenzenethiol and toluenethiol were obtained from Aldrich. Benzenethiol was from Tokyo Kasei Kogyo. These materials were purified by conventional methods before use.

The cobalt(IV) sulfide catalyst [31] was synthesized by the reaction of cobalt(II) chloride hexahydrate with sodium disulfide in aqueous solution. The nickel(IV) sulfide catalyst [31] was synthesized from nickel(II) sulfate hep-tahydrate and sodium disulfide in the same manner. These catalysts were crushed and sieved through 200-mesh before use.

 $CoCl_2 + Na_2S_2 \rightarrow CoS_2 + 2NaCl$

 $NiSO_4 + Na_2S_2 \rightarrow NiS_2 + Na_2SO_4$

A commercial HDS catalyst "CDS-R9", which was supplied by Chiyoda Kako, was a $CoO-MoO_3/\gamma$ -Al₂O₃ type. Before use, CDS-R9 was also crushed and sieved through 200-mesh and presulfided in a 100 ml autoclave at 320°C using hydrogen and sulfur powder.

Procedures and analyses

The reaction (0.02 mol reactant, 0.05 mol in hexadecane solution and 0.002 mol catalyst, except the sulfided CDS-R9 catalyst, 0.7 g) was carried out in a magnetically stirred autoclave (Sakashita Seisakusho SUS 304 volume 100 ml) at 120–320°C under constant hydrogen pressure of 40 atm for 90 min. The products obtained were analyzed by a gas chromatograph (Shimadzu 15A/C-R5A Chromatopac) using an OV-17 glass column with temperature programming and a flame ionization detector (FID). Since the details of both the reaction procedure and the analyses have been reported previously [30], only a brief description is given here.

MO calculation

The MINDO/3 calculations were carried out using the MOPAC version 6.01 [32] run on a Hitachi Super computer (HITAC M-680H) in the Computer Centre, the University of Tokyo. The starting geometries of the benzenethiols were obtained from the GUMMOS program version 4.17 [33]. The calculations were carried out by the standard MINDO/3 program based on the restricted Hartree-Fock (RHF) method. The geometries were optimized in internal coordinates and were terminated when the change in energy on successive iteration was less than 0.00001 kcal mol⁻¹ and the change in the density matrix elements on two successive iterations was less than 0.001.

Results and discussion

Hydrogenolysis of benzenethiols over cobalt(IV) sulfide catalyst

Though the reactions were carried out over a wide range of reaction temperatures, 120-280 °C, a typical result at 240 °C is shown in Fig. 1.

Benzenethiol(BT)

In the hydrogenolysis of BT, 18% benzene and 15% diphenylsulfide were mainly produced. Although the conversion of BT to benzene was increased to some extent with increased reaction temperature, the sum of the converted, hydrodesulfurized products was not quite 60% at a high temperature of 280 °C. These results show that BT is not more reactive than the ring substituted benzenethiols, which will be described below.

Aminobenzenethiols (ABT)

In the hydrogenolysis of ABT, the isomers gave aniline, bis(aminophenyl)sulfide and bis(aminophenyl)disulfide in every instance.

Whereas bis (aminophenyl) disulfide was chiefly formed at temperatures below 160°C, in the case of o-ABT, the HDS occurred sufficiently at 240°C and 87% aniline was formed. Under the same reaction conditions, on the other



Fig. 1. Hydrodesulfurization of benzenethiols over CoS_2 catalyst at 240°C. (\Box) Benzenethiol; (+) aminobenzenethiols; (\Diamond) methoxybenzenethiols; (Δ) toluenethiols.

hand, *m*-ABT was converted into aniline in 55% yield. *p*-ABT was most reactive and yielded 71% aniline even at 160° C.

It is clear that the HDS reactivities of the isomers decreased in the order $p-ABT \gg o-ABT > m-ABT$ at 160–240°C.

Methoxybenzenethiols (MBT)

Hydrogenolysis of the isomers of MBT occurred to a lesser extent than that of ABT at temperatures below 200° C, and a temperature over 240° C was required for sufficient reaction.

Ortho-MBT gave 41% methoxybenzene and 19% phenol as the main products at 240°C. At the same reaction temperature, *m*-MBT was converted to 24% methoxybenzene and 23% bis(3-methoxyphenyl)sulfide. In the case of the *p*-isomer, HDS proceeded sufficiently and produced methoxybenzene at 240°C. These results indicate that the reactivities of the isomers at 240°C decrease in the following order: *p*-MBT>o-MBT>*m*-MBT.

Also over the presulfided $Co-Mo/Al_2O_3$ catalyst, similar results of the reactivities have been reported [34].

Toluenethiols (TT)

For the isomers of TT over cobalt(IV) sulfide catalyst, toluene and bis(methylphenyl)sulfides were formed in every instance with a small degree of HDS conversion at 240°C. Therefore, a reaction temperature over 280°C was required for sufficient reaction.

Ortho-, meta- and para-isomers were converted to toluene in 29, 26 and 42% yields at 240°C, respectively. These results show that the HDS reactivities of the isomers of TT decrease in the order p-TT>o-TT>m-TT at this reaction temperature.

Furthermore, in connection with the reaction temperature for each substituent, it is clear that the HDS reactivities of both the *p*- and *o*-isomers decrease in the order: ABT \gg MBT \gg TT > BT. This order is in good agreement with that of Hammett's σ values for the substituents [35].

Hydrogenolysis of benzenethiols over nickel(IV) sulfide catalyst

Hydrogenolysis of BT and ring substituted benzenethiols was investigated over a wide range of reaction temperatures 120–320°C, and the representative results at 280°C are shown in Fig. 2

The HDS activity of the nickel catalyst for the benzenethiols is less than that of the cobalt catalyst except for p-ABT, which produced 27% aniline even at 120°C. Therefore a slightly higher reaction temperature was generally required for sufficient reaction. The kinds of reaction products in every instance were similar to those of the reactions where cobalt(IV) sulfide was used as a catalyst.

HDS reactivities of the isomers of the benzenethiols at 200-280°C were found to be in the order: p-ABT $\gg o$ -ABT> m-ABT; p-MBT> o-MBT> m-



Fig. 2. Hydrodesulfurization of benzenethiols over NiS₂ catalyst at 280°C. (\Box) Benzenethiol; (+) aminobenzenethiols; (\Diamond) methoxybenzenethiols; (Δ) toluenethiols.

MBT; p-TT>m-TT>o-TT. This order is quite similar to that of the cobalt catalyst except for the order between o- and m-TT. Such an opposite order for TT might be attributed to steric hindrance of the methyl group in the orthoposition, which may be also related to the lower HDS activity of the nickel catalyst. Concerning the reaction temperature, furthermore, the HDS reactivities of the p-isomers are found to be in the order ABT \gg MBT>TT>BT. This order of HDS reactivities is also the same as that when cobalt (IV) sulfide was used as the catalyst.

Hydrogenolysis over a presulfided commercial HDS catalyst

Hydrogenolysis over CDS-R9 catalyst was carried out for the *para*-substituted benzenethiols at 160-240 °C and the results are shown in Fig. 3.

Although a direct comparison of the HDS activity of the presulfided CDS-R9 catalyst with those of cobalt(IV) sulfide and nickel(IV) sulfide is of little significance, the results shown in Fig. 3 indicate that the catalyst generally shows high HDS activity towards the reactants used in this experiment; for example, *ca.* 82% *p*-ABT was converted into aniline even at 160°C.

It is well known that the group VIII transition metals in $Co-Mo/Al_2O_3$, Ni-Mo/Al₂O₃, or other bimetallic types of industrial HDS catalysts, enhance the HDS activity. Delmon [36] proposed the idea of the contact synergy model as the origin of enhancement, which causes modification of the electron density of the active sites. Relative to the active surface structure, Topsøe *et al.* [37] found that the Co-Mo-S or Ni-Mo-S type structure assumes an important role in bimetallic catalysts.



Fig. 3. Hydrodesulfurization of benzenethiols over presulfided CDS-R9 catalyst. (\Box) Benzenethiol; (+) *p*-aminobenzenethiol; (\diamondsuit) *p*-methoxybenzenethiol; (\bigtriangleup) *p*-toluenethiol.

Regarding the reaction temperature, the HDS reactivities of the substituted benzenethiols were found to be in the order p-ABT $\gg p$ -MBT at 160°C; p-MBT > p-TT at 200°C; and p-TT > BT at 240°C. In addition, these orders of the HDS reactivities coincide with those of the HDS reactivities when cobalt(IV) sulfide and nickel(IV) sulfide were used as the catalysts.

Effect of electronic states of reactants on the reactivity

In the hydrogenolysis of ABT and MBT, the HDS caused selective cleavage of the aromatic C-S bond without any ring hydrogenation and produced aniline and methoxybenzene (or phenol), respectively. It may be characteristic that both the hydrodenitrogenation of ABT and hydrodeoxygenation of MBT scarcely occurred under the present reaction conditions. Also, in the case of TT, HDS occurred similarly to that with ABT and MBT, and gave toluene as the major product.

As for ABT and MBT in the present study, the HDS reactivities of the isomers were observed to be in the order $p \rightarrow o \rightarrow m$ -isomer for all the catalysts. In the case of TT, over the cobalt(IV) sulfide and the presulfided commercial HDS catalyst, the order of the reactivities was the same as that for ABT and MBT.

Furthermore, the HDS reactivities of the *para*- and *ortho*-substituted benzenethiols were found to decrease in the order $ABT \gg MBT > TT > BT$. This order is the same as the HDS reactivities when molybdenum (VI) sulfide was used as the HDS catalyst [30] and reflects the magnitude of Hammett's sub-

	Bond	Bond length (Å)	Bond angle	Angle (degrees)
benzenethiol	S1-C2	1.749	S1-C2-C3	120.1
, SH	C2-C3	1.408	S2-C3-C4	120.0
	C3-C4	1.409	C3-C4-C5	120.0
7 2 3	C4-C5	1.406	C4-C5-C6	119.9
s Q,	C5-C6	1.406	C5-C6-C7	120.1
	C6-C7	1.407	C6-C7-C2	120.0
	C7-C2	1.408	C7-C2-C3	119.9

TABLE 1

	Bond le	engths	and be	ond ang	les for	benzenethiol
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stituent constants (σ values) [35] in the series of amino, methoxy and methyl groups, and hydrogen. In the hydroprocessing of the mono-substituted benzenes Ph-X, Moreau et al. [23,25,29] also found a good correlation between the rate constants of hydrogenolysis of C_{sp^2} -X bonds and the resonance parameters ($\sigma_{\rm R}$ values) of the substituents X, and concluded that the hydrogenolysis was favored by slightly electron-donating substituents (Cl, Br, or SH) rather than by highly electron-donating substituents (N or O). From this evidence, it is suggested that the HDS of the substituted benzenethiols is strongly affected by the presence of electron-releasing substituents such as amino, methoxy and methyl groups. Since the electronic properties of the ipso-carbon atom can be directly influenced by the presence of these substituents in orthoor para-position, a close agreement of the orders between the experimental HDS reactivities and the magnitudes of the electron-releasing properties of the substituents may further suggest electronic importance of the *ipso*-carbon atom in the reaction of the substituted benzenethiols. It may be worthwhile to focus on the electronic states of both the sulfur and the ipso-carbon atoms in order to obtain more detailed information about the electronic factors affecting the HDS reactivities.

From MINDO/3 molecular orbital calculations [38] for the substituted benzenethiols whose structures are shown in Table 1–4, the magnitudes of the frontier π -electron densities (FED) on the positions of both the *ipso*-carbon and the sulfur atoms, $2(C_{\rm C}^{\rm HOMO})^2$ and $2(C_{\rm S}^{\rm HOMO})^2$, are observed in the following orders:

On the sulfur atom:

p-ABT (0.023) > o-ABT (0.010) > m-ABT (0.003) p-MBT (0.044) > o-MBT (0.027) > m-MBT (0.009) o-TT (0.079) $\ge p$ -TT (0.077) = m-TT (0.077) BT (0.108)

On the *ipso*-carbon atom:

$$p-ABT(0.461) > o-ABT(0.331) > m-ABT(0.050)$$

 $p-MBT(0.535) > o-MBT(0.370) > m-MBT(0.088)$
 $p-TT(0.506) > o-TT(0.474) > m-TT(0.409)$
 $BT(0.520)$

Except for TT on the sulfur atom, these orders of the FED among the isomers of the substituted benzenethiols are in rough agreement with those of the actual HDS reactivities which might be promoted by the electron-releasing substituents in the *ortho-* and *para*-positions.

In a direct comparison of the FED, however, the remaining but very difficult subject is how to interpret the difference in reactivity among amino-,

TABLE 2

	Bond	Bond length (Å)	Bond angle or dihedral angle	Angle (degrees)
o-aminobenzenethiol	S1-C2	1.754	S1-C2-C3	120.8
	C2-C3	1.435	S2-C3-C4	119.0
	C3-C4	1.429	C3-C4-C5	119.6
і сн	C4-C5	1.404	C4-C5-C6	121.3
之 NH2	C5-C6	1.406	C5-C6-C7	119.3
	C6-C7	1.408	C6-C7-C2	121.0
5	C7-C2	1.403	C7-C2-C3	119.8
	N8-C3	1.351	N8-C3-C2	119.8
			N8-C3-C2-S1	0.5
<i>m</i> -aminobenzenethiol	S1-C2	1.749	S1-C2-C3	119.3
	C2-C3	1.405	S2-C3-C4	120.4
1	C3-C4	1.433	C3-C4-C5	118.2
SH	C4-C5	1.433	C4-C5-C6	120.3
² 🖳 ³	C5-C6	1.401	C5-C6-C7	120.8
6 NH2	C6-C7	1.407	C6-C7-C2	119.7
5 8 -	C7-C2	1.405	C7-C2-C3	120.5
	N8-C4	1.350	N8-C4-C3	121.0
			N8-C4-C3-C2	-179.8
p-aminobenzenethiol	S1-C2	1.746	S1-C2-C3	121.0
	C2-C3	1.408	S2-C3-C4	121.2
1	C3-C4	1.404	C3-C4-C5	121.0
SH	C4-C5	1.429	C4-C5-C6	117.4
7 (, ,	C5-C6	1.430	C5-C6-C7	120.6
6 4	C6-C7	1.402	C6-C7-C2	121.6
NH2	C7-C2	1.409	C7-C2-C3	118.2
o -	N8-C5	1.350	N8-C5-C4	121.4
			N8-C5-C4-C3	-179.9

Bond lengths, bond angles and dihedral angles for o-, m- and p-aminobenzenethiol

TABLE 3

Bond lengths, bond angles and dihedral angles for o-, m- and p-methoxybenzenethiol

	Bond	Bond length (Å)	Bond angle or dihedral angle	Angle (degrees)
o-methoxybenzenethiol	S1-C2	1.749	S1-C2-C3	117.5
	C2-C3	1.428	S2-C3-C4	119.8
	C3-C4	1.414	C3-C4-C5	119.2
1	C4-C5	1.410	C4-C5-C6	121.2
SH 6	C5-C6	1.401	C5-C6-C7	119.4
7 С 2 нз	C6-C7	1.413	C6-C7-C2	120.5
6 4 3	C7-C2	1.400	C7-C2-C3	119.8
5	O8-C3	1.327	O8-C3-C2	110.4
	C9-O8	1.344	C9-O8-C3	131.0
			O8-C3-C2-S1	0.3
			C9-O8-C3-C2	-178.1
<i>m</i> -methoxybenzenethiol	S1-C2	1.747	S1-C2-C3	119.7
-	C2-C3	1.406	S2-C3-C4	119.9
	C3-C4	1.427	C3-C4-C5	119.9
1	C4-C5	1.419	C4-C5-C6	119.1
SH L2	C5-C6	1.405	C5-C6-C7	121.2
7	C6-C7	1.405	C6-C7-C2	119.9
s 4 0	C7-C2	1.410	C7-C2-C3	120.0
5 I CH2	O8-C4	1.345	08-C4-C3	112.9
₉ 5	C9-08	1.340	C9-O8-C4	132.7
			O8-C4-C3-C2	-179.7
			C9-O8-C4-C3	-178.6
<i>p</i> -methoxybenzenethiol	S1-C2	1.747	S1-C2-C3	120.6
-	C2-C3	1.410	S2-C3-C4	121.7
	C3-C4	1.404	C3-C4-C5	119.4
SH	C4-C5	1.424	C4-C5-C6	119.4
2 2 3	C5-C6	1.419	C5-C6-C7	119.7
• () ·	C6-C7	1.407	C6-C7-C2	121.4
, <u>∖</u> 5	C7-C2	1.407	C7-C2-C3	118.4
H ₃ C ⁻⁰	O8-C5	1.325	O8-C5-C4	113.4
	C9-O8	1.340	C9-O8-C5	132.5
	-		08-C5-C4-C3	-179.7
			C9-O8-C5-C4	- 179.5

methoxyl- and methyl-substituted compounds and BT, since the orders of magnitude of the FED are in contrast to those of the actual HDS reactivities.

When the ratio of the FEDs on the *ipso*-carbon atom relative to that on the sulfur atom, $(C_{\rm C}^{\rm HOMO}/C_{\rm S}^{\rm HOMO})^2$, was calculated for the ring substituted benzenethiols, some interesting facts were found. As seen in Fig. 4, these values are in good agreement with the experimental results, except for the reverse order between *ortho*- and *para*-isomers of ABT and MBT, which may be attributed to steric hindrance of the substituent in the *ortho*-position. The order

TABLE 4

	Bond	Bond length (Å)	Bond angle or dihedral angle	Angle (degrees)
o-toluenethiol	S1-C2	1.751	S1-C2-C3	121.1
	C2-C3	1.427	S2-C3-C4	116.1
	C3-C4	1.427	C3-C4-C5	123.0
人。	C4-C5	1.404	C4-C5-C6	119.5
⁷ () ³	C5-C6	1.404	C5-C6-C7	119.1
6 <u>5</u> 4	C6-C7	1.404	C6-C7-C2	121.4
-	C7-C2	1.408	C7-C2-C3	120.9
	C8-C3	1.492	C8-C3-C2	122.4
			C8-C3-C2-S1	0.4
<i>m</i> -toluenethiol	S1-C2	1.749	S1-C2-C3	119.9
⁵ ¹² ² ³ ⁴ ⁵ ¹² ¹² ¹² ¹² ¹³ ¹⁴ ¹² ¹⁵ ¹² ¹⁵ ¹² ¹² ¹² ¹² ¹² ¹² ¹² ¹²	C2-C3	1.406	S2-C3-C4	122.5
	C3-C4	1.427	C3-C4-C5	115.6
	C4-C5	1.425	C4-C5-C6	122.3
	C5-C6	1.404	C5-C6-C7	120.4
	C6-C7	1.406	C6-C7-C2	119.0
	C7-C2	1.407	C7-C2-C3	120.1
	C8-C4	1.491	C8-C4-C3	122.1
			C8-C4-C3-C2	-179.2
<i>p</i> -toluenethiol $\stackrel{^{1}}{\overset{^{1}}{\underset{6}{\overset{^{1}}{\bigcup_{5}}}}}$	S1-C2	1.747	S1-C2-C3	120.7
	C2-C3	1.408	S2-C3-C4	120.2
	C3-C4	1.406	C3-C4-C5	122.8
	C4-C5	1.425	C4-C5-C6	115.1
	C5-C6	1.424	C5-C6-C7	122.7
	C6-C7	1.405	C6-C7-C2	120.4
ĊH3	C7-C2	1.406	C7-C2-C3	118.7
U.	C8-C5	1.491	C8-C5-C4	122.4
			C8-C5-C4-C3	179.4

Bond lengths, bond angles and dihedral angles for o-, m- and p-toluenethiol

of the ratio described above in heterocyclic sulfur compounds (i.e., phenothiazine, thianthrene, thioxanthene and dibenzothiophene) is also in agreement with that of the HDS reaction rates which were measured by Aubert and coworkers [19-21].

Although comparison of reactivities such as FED among molecules that have different substituents is not generally allowed, the ratios of the two FEDs seem to reflect well the intermolecular differences in reactivity described above. On the other hand, the order of energy levels of the highest occupied π -orbital (π -HOMO) is quite similar to the HDS reactivities of aromatic sulfur compounds, as shown in Fig. 5. Correlation between the energy level of π -HOMO and HDS reactivity may be interpreted from the fact that absorbates whose HOMO is high interact with the unoccupied *d* band of MoS₂ easily [39].

This coincidence of the two phenomena suggests that both quantities of



Fig. 4. Ratios of the frontier electron densities (FED) of the *ipso*-carbon atom to the sulfur atom for benzenethiols. (\Box) Benzenethiol; (+) aminobenzenethiols; (\diamondsuit) methoxybenzenethiols; (\triangle) toluenethiols.



Fig. 5. Energy levels of π -HOMO for benzenethiols. (\Box) Benzenethiol; (+) aminobenzenethiols; (\diamond) methoxybenzenethiols; (\triangle) toluenethiols.

the ratio of FEDs and the energy level can be called theoretical reactivity indices. This new reactivity index defined as a trial seems at least to suggest that the HDS reactivities of the ring substituted benzenethiols are not independently but concertedly effected by the magnitudes of FEDs on the positions of both the sulfur and the *ipso*-carbon atoms.

It is regrettable that there is no idea of how to connect this theoretically calculated index to the HDS reactivity of the absorbates under the present conditions.

The back donation of an electron from the d orbital of the transition metals to the LUMO of the absorbate will be examined in a future paper.

Conclusion

HDS of ring substituted benzenethiols over CoS_2 , NiS_2 and a presulfided commercial HDS catalyst (CDS-R9) were promoted by the presence of electron-releasing substituents in *ortho* and *para* positions.

These promoting effects of the substituents on the HDS, therefore, are confirmed to be a general phenomenon which is almost independent of the kind of catalyst, because the aspects of the reactivities described above are quite similar to the reactivities over a MoS_3 catalyst [30].

From the MINDO/3 calculations, the differences in the reactivity among the isomers of the substituted benzenethiols is correlated roughly with the FEDs on the positions of both the *ipso*-carbon and the sulfur atoms.

The orders of the magnitude of both the newly defined indices $(C_{\rm C}^{\rm HOMO}/C_{\rm S}^{\rm HOMO})^2$ and the energy levels of π -HOMO, on the other hand, are in good agreement with the HDS reactivities.

Thus it is suggested that both the energy levels and the FEDs of the reactants assume an important role in the HDS reactivities of the ring substituted benzenethiols and that the magnitudes of the FEDs on the positions of both the *ipso*-carbon and the sulfur atoms affect the reactivities not independently but concertedly.

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