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Hydroprocessing of Dibenzothiophene, Phenothiazine, Phenoxathiin, Thianthrene, and Thioxanthene on a Sulfided $NiO–MoO_3/\gamma\text{-}Al_2O_3$ Catalyst[1]

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The hydroprocessing of phenothiazine, phenoxathiin, thianthrene, and thioxanthene was studied by a batch method at 340°C and 70 bar H_2 over a sulfided $NiO–MoO_3/\gamma\text{-}Al_2O_3$ catalyst. The hydrodesulfurization (HDS) rate constants are similar to one another and about tenfold higher than that of dibenzothiophene. The presence of a second heteroatom or a methylene group does not play an important role on the removal of sulfur. The differences of reactivity could rather result from geometrical considerations in relation with the ease of adsorption on the catalyst surface. The cleavage patterns and reaction networks for the hydroprocessing of compounds dibenzothiophene, phenothiazine, phenoxathiin, thianthrene, and thioxanthene are discussed. The product distribution allows, in particular, an estimate to be made of the rates of hydrogenation and hydrogenolysis in HDS, hydrodenitrogenation (HDN), and hydrodeoxygenation (HDO) processes.

INTRODUCTION

Catalytic hydrodesulfurization of petroleum fractions, shale oils, or coal oils occurs concurrently with the removal of nitrogen and oxygen. Consequently, simultaneous reactions HDS/HDN, HDS/HDO, and HDN/HDO were extensively studied during recent years (*1–6*) but few studies were reported concerning HDS reactions where a second heteroatom is present on the same molecule.

Nagai and Sakikawa (*7*) reported the hydrogenolysis of phenothiazine, phenoxathiin, and thianthrene over a sulfided $CoO–MoO_3/\gamma\text{-}Al_2O_3$ catalyst but no kinetic data were available.

More recently, Kwart *et al.* (*8*) reported a comparative study of the hydroprocessing of phenothiazine and dibenzothiophene catalyzed by a sulfided $CoO–MoO_3/\gamma\text{-}Al_2O_3$. It was found that at 300°C and 70 bar H_2 the hydrodesulfurization of phenothiazine occurred ten times more rapidly than the hydrodesulfurization of dibenzothiophene. Such a behavior was not expected as nitrogen-containing species are generally known to inhibit HDS processes under simultaneous reaction conditions. In order to explain their experimental results the authors suggested a flat, multipoint or ring adsorption in such a manner that the nitrogen atom is strongly involved and strongly facilitates the adsorption. However, in our opinion, these explanations cannot satisfactorily account for the particular behaviour of phenothiazine as compared to dibenzothiophene, since two points, at least, were not considered, namely (i) the influence of the folding of the molecules and (ii) the basicity of the second heteroatom. It is well established that (i) phenothiazine is folded along the S–N axis with a dihedral angle of 140° between the two aromatic rings (*9*)

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[1] Part of this work was presented at the 2nd Workshop on Hydrotreating Catalysts held in Louvain-la-Neuve, Belgium (1984).

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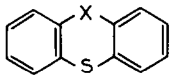
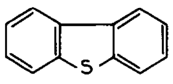
while dibenzothiophene is planar (*10*), and (ii) the nitrogen atom is less basic when bound to two phenyl groups (pK_a = 0.79 for diphenylamine compared to pK_a = 4.60 for aniline and pK_a = 10.64 for the saturated stronger base cyclohexylamine (*11*)).

These structural and electronic effects were partly studied in our laboratory by carrying out the hydroprocessing of phenothiazine, thianthrene, and dibenzothiophene over a sulfided $NiO–MoO_3/\gamma-Al_2O_3$ catalyst where it was found that HDS of phenothiazine and thianthrene, respectively, occurred 7-fold and 20-fold more rapidly than HDS of dibenzothiophene at 250°C and 40 bar H_2 (*12*).

In order to complete this preliminary work, we have investigated in the present paper the hydroprocessing of phenothiazine (**1**), phenoxathiin (**2**), thianthrene (**3**), thioxanthene (**4**), and dibenzothiophene (**5**), on a sulfided $NiO–MoO_3/\gamma-Al_2O_3$ catalyst at 340°C and 70 bar. From the comparison of these compounds where N is replaced by O, S, or a methylene group we expect to have more information concerning the different factors which affect HDS, HDO, and HDN reactions.



1 X = NH Phenothiazine
2 X = O Phenoxathiin
3 X = S Thianthrene
4 X = CH_2 Thioxanthene



5 Dibenzothiophene

EXPERIMENTAL

The catalyst used was Procatalyse HR 346, which has the following composition: 3% NiO, 14% MoO_3, and 83% Al_2O_3. It was sulfided at atmospheric pressure using a fluidized-bed technique with a gas mixture of 15% H_2S and 85% H_2 by volume. The catalyst (5 g, particle size 0.100–0.125 mm) was heated in flowing H_2/H_2S (gas flow: 120 ml/min) from 20 to 400°C (8°C/min) and held at 400°C for 4 h, then cooled and finally swept with nitrogen for 30 min.

Experiments were carried out in a 0.3-liter stirred autoclave (Autoclave Engineers type Magne-Drive), operating in a batch mode and equipped with a system for sampling of liquid during the course of the reaction without stopping the agitation.

Typical procedure was as follows: a 0.1 *M* solution of organic reactant in 80 ml of decane (analytical grade) was poured into the autoclave. The sulfided catalyst (0.8 g) was then added to this solution. After purging with nitrogen, the temperature was increased under nitrogen until it reached 340°C. Nitrogen was then removed and hydrogen was introduced at the required pressure (70 bar). Zero time was taken when the agitation began.

Starting materials were either commercially available compounds (phenothiazine, thianthrene, phenoxazine, and xanthene) or were prepared according to standard procedures (phenoxathiin (*13*) and thioxanthene (*14*)).

Analyses were performed on a Girdel 30 gas chromatograph equipped with a flame ionization detector using nitrogen as carrier gas. The column used was OV 17 3% on Chromosorb Q 80/100, 3 m × $\frac{1}{8}$ in. Products were identified by comparison with authentic samples and GC–MS analysis.

The rate constants were deduced from the experimental curves by curve fitting and simulation using a HP 9820 computer with a HP 9826A tracing table, assuming all the reactions to be first order in the organic reactant. The calculated reaction rate constants (in min^{-1}) depend on the weight of catalyst and are then referred to 1 g of catalyst.

RESULTS

Dibenzothiophene

The hydrodesulfurization of dibenzothiophene, a representative model of the species present in the heavy feedstock, has often been studied under various experimen-

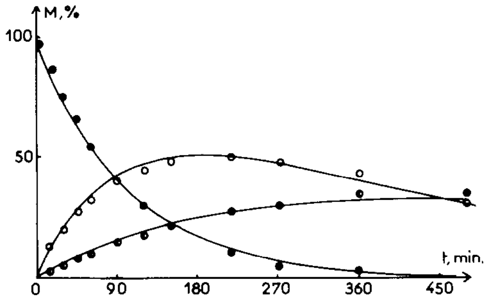


FIG. 1. Product distribution vs time for hydroprocessing of dibenzothiophene over sulfided NiO–$MoO_3/\gamma\text{-}Al_2O_3$ at 340°C and 70 bar H_2. Dibenzothiophene (●), biphenyl (○), cyclohexylbenzene (◐).

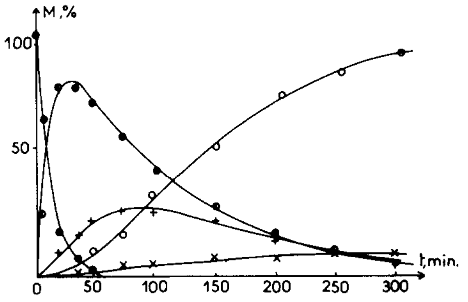
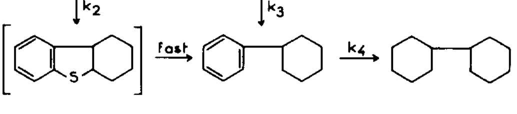


FIG. 2. Product distribution vs time for hydroprocessing of phenothiazine over sulfided NiO–$MoO_3/\gamma\text{-}Al_2O_3$ at 340°C and 70 bar H_2. Phenothiazine (●), diphenylamine (◐), aniline (+), benzene (×), cyclohexane (○).

tal conditions to elucidate the behavior of high-molecular-weight aromatic sulfur compounds (*1*, *15–22*).

In the present work, the hydrodesulfurization of dibenzothiophene over a sulfided NiO–$MoO_3/\gamma\text{-}Al_2O_3$ catalyst at 340°C and 70 bar H_2 yielded biphenyl and cyclohexylbenzene as the major products. The concentration vs time plots for dibenzothiophene hydroprocessing are given in Fig. 1. The curves drawn in Fig. 1 are computer-simulated based on a parallel reaction network for the formation of biphenyl and cyclohexylbenzene as shown in Scheme 1.

The value of the individual rate constants resulting from this kinetic parallel scheme are the following: $k_1 = 9 \times 10^{-3}$, $k_2 = 2 \times 10^{-3}$, $k_3 = 3 \times 10^{-3}$, and $k_4 = 3 \times 10^{-3}$ $min^{-1} \cdot (g \cdot cat.)^{-1}$, the total rate constant for HDS of dibenzothiophene being equal to $k_1 + k_2$. It should be noted that the rate constants of biphenyl hydrogenation are slightly different depending on whether biphenyl acts as an intermediate or a starting material; the values are 3×10^{-3} $min^{-1} \cdot (g \cdot cat.)^{-1}$ in the former case and 6×10^{-3} $min^{-1} \cdot (g \cdot cat.)^{-1}$ in the latter one (*23*). Biphenyl hydrogenation would be moderately inhibited by H_2S resulting from the hydrodesulfurization step in agreement with the previous observations of Broderick *et al.* (*15*) over a sulfided CoO–$MoO_3/\gamma\text{-}Al_2O_3$ catalyst.



SCHEME 1. Reaction Network for Hydroprocessing of Dibenzothiophene on Sulfided NiO–$MoO_3/\gamma\text{-}Al_2O_3$ at 340°C and 70 bar H_2.

Phenothiazine

The hydroprocessing of phenothiazine was previously studied on a sulfided CoO–$MoO_3/\gamma\text{-}Al_2O_3$ catalyst by Kwart *et al.* (*8*) and on sulfided NiO–$MoO_3/\gamma\text{-}Al_2O_3$ and NiO–$WO_3/\gamma\text{-}Al_2O_3$ catalysts in our laboratory (*12*, *24*).

In the present work, the hydrodesulfurization of phenothiazine rapidly yields diphenylamine as the major product which can then undergo hydrogenation and hydrogenolysis to give benzene and cyclohexane as final products (under the experimental conditions used here, the hydrogenation of benzene into cyclohexane cannot compete in a significant manner with the other steps).

The concentrations vs time plots for phenothiazine hydroprocessing are given in Fig. 2; those for the hydroprocessing of diphenylamine are given in Fig. 3. The curves drawn in Figs. 2 and 3 are computer-simulated based on the reaction network shown in Scheme 2.

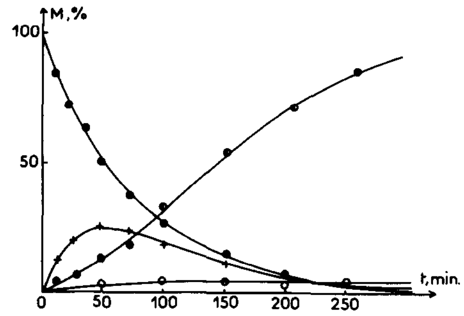


FIG. 3. Product distribution vs time for hydroprocessing of diphenylamine over sulfided NiO–MoO_3/γ-Al_2O_3 at 340°C and 70 bar H_2. Diphenylamine (●), aniline (+), benzene (O), cyclohexane (◐).

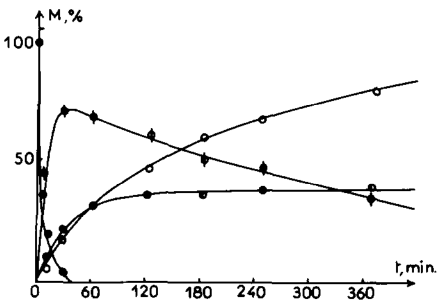
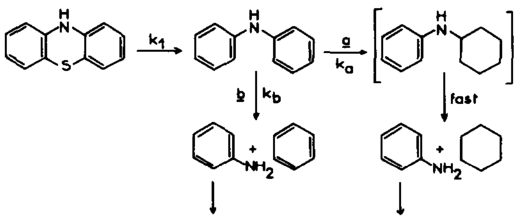


FIG. 4. Product distribution vs time for hydroprocessing of phenoxathiin over sulfided NiO–MoO_3/γ-Al_2O_3 at 340°C and 70 bar H_2. Phenoxathiin (●), diphenyl ether (∅), benzene (◐), cyclohexane (O).

It should be noted that the reaction network given in Scheme 2 is also observed for a sulfided NiO–WO_3/γ-Al_2O_3 catalyst (*24*) but differs from the consecutive reaction network proposed by Kwart *et al.* on a sulfided CoO–MoO_3/γ-Al_2O_3 catalyst under similar conditions of temperature and hydrogen pressure (*8*). The individual rate constants of the different steps are the following: $k_1 = 140 \times 10^{-3}\ \mathrm{min}^{-1} \cdot (\mathrm{g} \cdot \mathrm{cat.})^{-1}$ for the disappearance of phenothiazine and $k_2 = k_a + k_b = 10 \times 10^{-3}\ \mathrm{min}^{-1} \cdot (\mathrm{g} \cdot \mathrm{cat.})^{-1}$ for the disappearance of diphenylamine. The rate constant for the hydroprocessing of aniline over sulfided NiO–MoO_3/γ-Al_2O_3 equals $11 \times 10^{-3}\ \mathrm{min}^{-1} \cdot (\mathrm{g} \cdot \mathrm{cat.})^{-1}$ with cyclohexane as the major product (~95%).

By assuming that the conversion of benzene into cyclohexane cannot compete in a significant manner with the other steps, it is possible to estimate the rates of hydrogenation and hydrogenolysis of diphenylamine from the concentrations of benzene and cyclohexane (10 and 90%, respectively) formed after the complete disappearance of diphenylamine. The rate ratio hydrogenation/hydrogenolysis is about 9, thus confirming that hydrogenation of aromatic rings is required prior to any C–N bond cleavage.



SCHEME 2. Reaction Network for Hydroprocessing of Phenothiazine on Sulfided NiO–MoO_3/γ-Al_2O_3 at 340°C and 70 bar H_2.

Phenoxathiin

The first step of the hydroprocessing of phenoxathiin over a sulfided NiO–MoO_3/γ-Al_2O_3 catalyst at 340°C and 70 bar H_2 is a rapid desulfurization to give diphenyl ether followed by either hydrogenation or hydrogenolysis to yield cyclohexane and benzene as final products. Here also, the hydrogenation of benzene into cyclohexane cannot compete in a significant manner with the other steps.

The concentrations vs time plots for phenoxathiin hydroprocessing are given in Fig. 4, and those for diphenyl ether hydroprocessing are given in Fig. 5. The curves drawn in Figs. 4 and 5 are computer-simulated based on the reaction network shown in Scheme 3. The individual rate constants of the different steps are $k_1 = 150 \times 10^{-3}\ \mathrm{min}^{-1} \cdot (\mathrm{g} \cdot \mathrm{cat.})^{-1}$ for desulfurization of phenoxathiin and $k_2 = k_a + k_b = 6 \times 10^{-3}\ \mathrm{min}^{-1} \cdot (\mathrm{g} \cdot \mathrm{cat.})^{-1}$ for the disappearance of diphenyl ether.

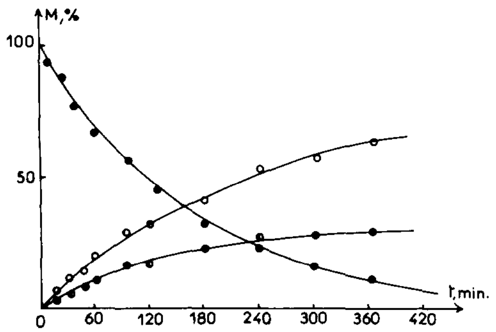
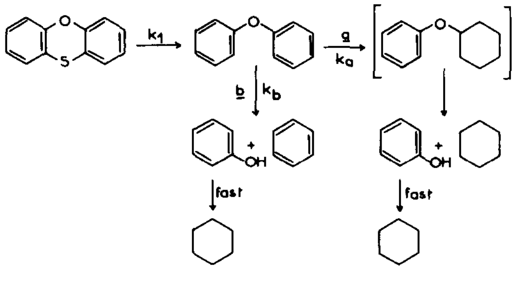


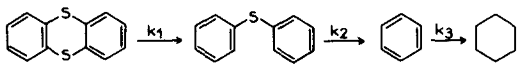
FIG. 5. Product distribution vs time for hydroprocessing of diphenyl ether over sulfided NiO–MoO$_3$/γ-Al$_2$O$_3$ at 340°C and 70 bar H$_2$. Diphenyl ether (●), benzene (◐), cyclohexane (○).

The postulated intermediates phenylcyclohexyl ether and phenol, which are not detected during hydroprocessing of phenoxathiin or diphenyl ether, were also studied under the same experimental conditions. Phenylcyclohexyl ether is mainly converted into phenol and cyclohexene during the heat-up time. The halftime for the disappearance of the remaining phenylcyclohexyl ether under 70 bar H$_2$ at 340°C is about 2–3 min, so that this intermediate cannot accumulate enough to be detected. In a similar way, phenol cannot be detected as its rate of disappearance is much higher (35 × 10^{-3} min^{-1} · (g · cat.)$^{-1}$) than its rate of formation (6 × 10^{-3} min^{-1} · (g · cat.)$^{-1}$). It should be noted that the hydrogenation of phenol yields cyclohexane only.

By assuming that the conversion of benzene into cyclohexane cannot compete in a significant manner with the other steps, the rates of hydrogenation and hydrogenolysis can be estimated, as previously shown in the case of diphenylamine hydroprocessing, from the concentrations of cyclohexane and benzene (66 and 33%, respectively) formed after the complete disappearance of diphenyl ether. By taking into account the concentration of cyclohexane resulting from the hydrogenolysis path *b* (Scheme 3) the rate ratio hydrogenation/hydrogenolysis is about 1 for diphenyl ether hydroprocessing.



SCHEME 3. Reaction Network for Hydroprocessing of Phenoxathiin on Sulfided NiO–MoO$_3$/γ-Al$_2$O$_3$ at 340°C and 70 bar H$_2$.



SCHEME 4. Reaction Network for Hydroprocessing of Thianthrene on Sulfided NiO–MoO$_3$/γ-Al$_2$O$_3$ at 340°C and 70 bar H$_2$.

Thianthrene

The reaction network proposed in our laboratory for the hydrodesulfurization of thianthrene on a sulfided NiO–MoO$_3$/γ-Al$_2$O$_3$ catalyst at 250°C and 40 bar H$_2$ is given in Scheme 4 (*19*).

The individual rate constants k_1 and k_2 under these conditions were 1.5 × 10^{-2} and 11 × 10^{-2} min^{-1} · (g · cat.)$^{-1}$, respectively. Under the reaction conditions used in the present work (340°C and 70 bar H$_2$) diphenyl sulfide cannot be detected as an intermediate and benzene is observed as the major product (Fig. 6). The pseudo-first-order rate constant for the hydrodesulfurization

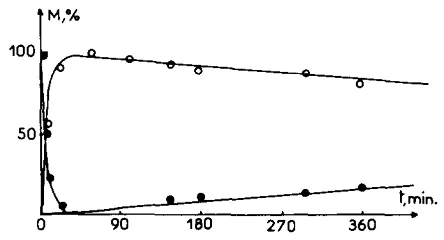


FIG. 6. Product distribution vs time for hydroprocessing of thianthrene over sulfided NiO–MoO$_3$/γ-Al$_2$O$_3$ at 340°C and 70 bar H$_2$. Thianthrene (●), benzene (◐), cyclohexane (○).

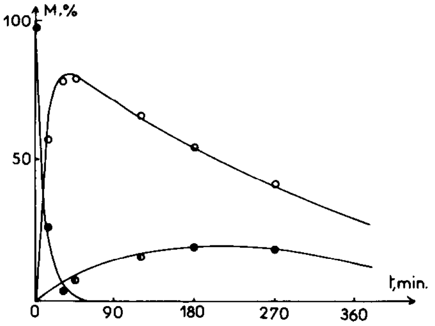


FIG. 7. Product distribution vs time for hydroprocessing of thioxanthene over sulfided NiO–MoO$_3$/γ-Al$_2$O$_3$ at 340°C and 70 bar H$_2$. Thioxanthene (●), phenylcyclohexylmethane (◐), diphenylmethane (○).

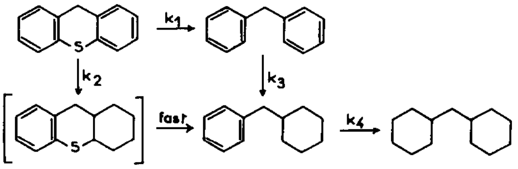
of thianthrene k_1 is 150 × 10^{-3} min^{-1} · (g · cat.)$^{-1}$.

It is worth noting that the rate of hydrogenation of benzene into cyclohexane also decreases when benzene acts as an intermediate, $k_3 = 0.5 \times 10^{-3}$ min^{-1} · (g · cat.)$^{-1}$ instead of 2 × 10^{-3} min^{-1} · (g · cat.)$^{-1}$ when benzene acts as starting material (*23*). As previously discussed for biphenyl hydrogenation, the hydrogenation of benzene would be moderately inhibited by H$_2$S resulting from the two desulfurization steps.

Thioxanthene

The hydrodesulfurization of thioxanthene over a sulfided NiO–MoO$_3$/γ-Al$_2$O$_3$ catalyst at 340°C and 70 bar H$_2$ yields mainly diphenylmethane which is then hydrogenated to phenylcyclohexylmethane. The concentrations vs time plots for the hydroprocessing of thioxanthene are given in Fig. 7.

The curves drawn in Fig. 7 are based on a parallel reaction network as illustrated in Scheme 5. The individual rate constants of the different steps are $k_1 = 100 \times 10^{-3}$, $k_2 = 2 \times 10^{-3}$, $k_3 = 3 \times 10^{-3}$, and $k_4 = 9 \times 10^{-3}$ min^{-1} · (g · cat.)$^{-1}$. It should be noted that the difference between parallel and consecutive networks is rather small. Nevertheless, the best correlations are obtained with the former network.



SCHEME 5. Reaction Network for Hydroprocessing of Thioxanthene on Sulfided NiO–MoO$_3$/γ-Al$_2$O$_3$ at 340°C and 70 bar H$_2$.

The moderate inhibiting effect of H$_2$S observed in the hydrogenation of biphenyl and benzene acting as intermediates instead of starting materials is less evident; the rate constants of hydrogenation are nearly identical within the experimental errors.

DISCUSSION

Hydrodesulfurization

The comparison of the HDS rates of phenothiazine and dibenzothiophene led Kwart *et al.* (*8*) to suppose a flat, multipoint or ring adsorption in such a manner that the nitrogen atom is highly involved and, through its basicity, strongly facilitates the adsorption. As seen in Table 1, this explanation is no longer valid since the replacement of nitrogen by sulfur, oxygen, or a methylene group does not affect the HDS rates in a significant manner. As seen also in Table 1, phenothiazine, phenoxathiin, thianthrene,

TABLE 1

HDS Rate Constants and Values of Dihedral Angles between the Two Aromatic Rings for Compounds **1–5** over Sulfided NiO–MoO$_3$/γ-Al$_2$O$_3$ at 340°C and 70 bar H$_2$

Compound	HDS rate constants[a,b] (10^{-3} min^{-1} · (g · cat.)$^{-1}$)	Dihedral angles
1 Phenothiazine	140	140°
2 Phenoxathiin	130	138°
3 Thianthrene	150	128°
4 Thioxanthene	110	135°
5 Dibenzothiophene	12	180°

[a] Data from Ref. (*25*).

[b] Experimental error: ~10% depending on the mode of calculation of the rate constants, by fixing, or not, the initial concentration in reactant.

TABLE 2

Hydroprocessing of Diphenyl Sulfide, Diphenyl Ether, Diphenylamine, Phenol, and Aniline over Sulfided NiO–MoO_3/γ-Al_2O_3 Catalyst at 340°C and 70 bar H_2. Reaction Percentages and Rate Constants for Hydrogenation and Hydrogenolysis

Compound	Hydrogenation		Hydrogenolysis	
	% Reaction	Rate constant[a]	% Reaction	Rate constant[a]
Diphenyl Sulfide	0	≅0	100	≅400
Diphenyl Ether	50	3	50	3
Diphenylamine	90	9	10	1
Phenol	>95	33	<5	≅2
Aniline	>90	10	<10	≅1

[a] Rate constant × 10^3 $min^{-1} \cdot (g \cdot cat.)^{-1}$.

and thioxanthene are folded along the S–X axis (X = N, O, S, CH_2) in a similar way. These results could be better explained in terms of an "anchor effect" and we have recently proposed that the rate enhancement could result from the energy differences between the adsorbed state and the transition state which would depend on whether the molecules are folded or planar (*25*). The adsorbed state should be more stabilized for planar molecules than for folded ones, increasing the difference of energy between the adsorbed state and the transition state.

Hydrogenation vs hydrogenolysis

From the relative concentrations of products benzene and/or cyclohexane formed during the hydroprocessing of diphenyl sulfide, diphenyl ether, diphenylamine, phenol, and aniline it is possible to estimate the respective ratios of hydrogenation and hydrogenolysis (Table 2). These results confirm that aromatic amines generally require hydrogenation prior to any C–N bond cleavage. Diphenylamine and aniline behave in a similar manner for hydrogenation, hydrogenolysis partitioning and rate constants (Table 2). On the other hand, the oxygenated compounds diphenyl ether and phenol behave differently. The calculated rate constants for C–O bond hydrogenolysis are similar (Table 2) whereas the rate of hydrogenation of phenol is about ten times higher than the hydrogenation rate of diphenyl ether, which naturally leads to large differences in partitioning, phenol yielding cyclohexane as the major product. As a consequence, one must be careful when attempting to establish reactivity orders for hydrogenation and hydrogenolysis of C–O and C–N bonds.

CONCLUSIONS

In the present work we have obtained new results concerning the electronic and geometric factors which affect HDS processes in the presence, on the same molecule, of a second heteroatom, N, O, S, or of a methylene group. Moreover, the product distribution allows an estimate of the rates of hydrogenation and hydrogenolysis in HDS, HDN, and HDO reactions.

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