Hydroprocessing of Phenothiazine Catalyzed by Co–Mo/γ-Al_2O_3

Harold Kwart,* James Katzer,*† and James Horgan

Center for Catalytic Science and Technology, Departments of Chemical Engineering and Chemistry, University of Delaware, Newark, Delaware 19711 *(Received: September 1, 1981; In Final Form: December 29, 1981)*

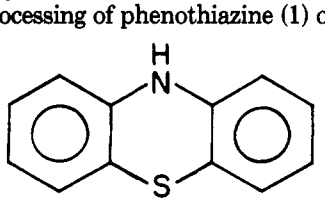
The hydroprocessing of phenothiazine catalyzed by sulfided Co–Mo/γ-Al_2O_3 was studied in a batch autoclave at 573 K and 6.89×10^6 Pa. Hydrodesulfurization (HDS) occurs much more rapidly than hydrodenitrogenation (HDN) and occurs 10-fold more rapidly than hydrodesulfurization of dibenzothiophene (a similar sulfur-containing compound) and 50-fold more rapidly than hydrodesulfurization of dibenzothiophene with an equimolar concentration of acridine. A one-point adsorption model for the reaction mechanism cannot explain the data; a flat, ring adsorption enhanced by strong involvement of the electrons of the nitrogen atom and with partial hydrogenation followed by β elimination is strongly favored.

Introduction

This study was undertaken for the purpose of evaluating the so-called one-point mechanism of hydrodesulfurization (HDS) of thiophenic compounds.[1] This reaction pathway, which postulates an initial end-on, one-site chemisorption of the thiophenic sulfur at the active site, also assumes that hydrogenolysis involves a series of hydrogen transfers to the carbon atoms bonded to the adsorbed thiophenic sulfur. These events are viewed in the reaction scheme in Figure 1. Although HDS catalysts are known to be very active in the hydrogenation of aromatic, conjugated, and isolated double-bond systems, the mechanisms of such hydrogenations have previously been thought to be separate and unrelated to the hydrogenolysis capabilities of the catalyst. There is considerable speculation in the literature that the hydrogenation and hydrogenolysis reactions occur at distinctly different sites on the sulfided molybdenum-containing catalysts.[2] The mechanism of Figure 1 obviously subscribes to this thesis in that it shows a possible pathway for hydrogenolysis of an unsaturated carbon–sulfur bond without any hydrogenation of the thiophene ring.

An alternative mechanism for thiophene HDS[3] (Figure 2) has been advanced which postulates that hydrogenation of at least one double bond of the thiophenic ring (taking place in the transition state **3**) is required before rupture of the carbon–sulfur bond can be realized. The bond-breaking step is visualized as a catalyst-assisted β elimination (shown in **4**) forming a coordinated butadiene sulfide, **5**. This step is rapidly succeeded by a nonspecific hydrogenation which can also be effected by H_2S. This restores the catalyst to its initial state, prepared for hydrogenation of another double bond if the mercaptobutadiene product **6** is readsorbed. This mechanism (Figure 2) assigns to the coordinatively unsaturated molybdenum center the function of double-bond hydrogenation;[3] the proposed structure is shown as **2**.

The hydroprocessing of phenothiazine (**1**) over a sulfided



Co–Mo/γ-Al_2O_3 catalyst provides a crucial test of the rival mechanistic proposals, Figures 1 and 2. This can be perceived by means of the following analyses (respectively) based on the competing mechanisms.

In phenothiazine (**1**) the highly electronegative nitrogen has significantly diminished the electron density on sulfur to below that in dibenzothiophene. Inductive effects of this nature are commonly recognized to influence electron availability (basicity) at heteroatom centers in heterocyclic compounds. Moreover, the nitrogen center exhibits somewhat greater electron density than in acridine or carbazole because the less electronegative, highly polarizable, transannular sulfur atom in **1** tolerates charge deficiency much better than carbon or nitrogen. On the other hand, both the N and S atoms in **1** can be regarded as strongly overlapped with both benzene rings in resonance interactions that result in highly increased electron densities on the rings and correspondingly decreased electron availability at the heteroatom centers.

On the basis of these considerations, the one-point adsorption reaction mechanism (Figure 1) would predict weakened adsorption of the sulfur in **1** to the anionic vacancy on the Mo^{4+} site postulated to be the active center, and thus a diminished HDS rate would be expected compared to dibenzothiophene. An even greater diminution in the HDS rate of phenothiazine vs. that of dibenzothiophene could be expected to result from the known inhibitory effect of nucleophilic nitrogen-containing compounds such as **1**.

Conversely, the multipoint adsorption reaction mechanism (Figure 2) anticipates that the facility of the HDS reaction is related to the strength of adsorption and ease of hydrogenation of one of the aromatic rings. Since in **1** the N and S centers should *enhance the strength of adsorption of the benzenoid rings* through their reinforcing resonance effects, the rate of ring hydrogenation, and therefore the HDS rate as well, should surpass that of both dibenzothiophene and diphenylamine.

Experimental Methods

The experiments were carried out in a 300-cm^3 stirred autoclave (Autoclave Engineers) which was operated in the batch mode. A special injection system was attached to

†Central Research Department, Mobil Research and Development Corp., Princeton, NJ 08540.

(1) Lipsch, J. M. J. G.; Schuit, G. C. A. *J. Catal.* **1969**, *15*, 179.
(2) (a) Kirsch, F. W.; Heineman, H.; Stevenson, D. H. *Ind. Eng. Chem.* **1957**, *49*, 646. (b) Komarewsky, V. I.; Knaggs, E. A. *Ibid.* **1951**, *43*, 1415. (c) Owens, P. J.; Amberg, C. H. *Can. J. Chem.* **1962**, *40*, 941, 947; *Adv. Chem. Ser.* **1961**, *33*, 182. (d) Desikan, P.; Amberg, C. H. *Can. J. Chem.* **1963**, *41*, 1966; **1964**, *42*, 843. (e) Kieran, P.; Kemball, C. *J. Catal.* **1965**, *4*, 380, 394. (f) Cowley, S. W. Ph.D. Thesis, Southern Illinois University, Carbondale, IL, 1975.
(3) Kwart, H.; Schuit, G. C. A.; Gates, B. C. *J. Catal.* **1980**, *61*, 128.

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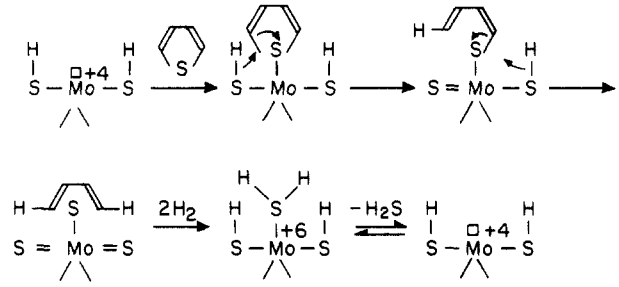

Figure 1. One-point adsorption reaction mechanism of thiophene HDS on sulfided Co-Mo/Al_2O_3 and related catalyst compositions.

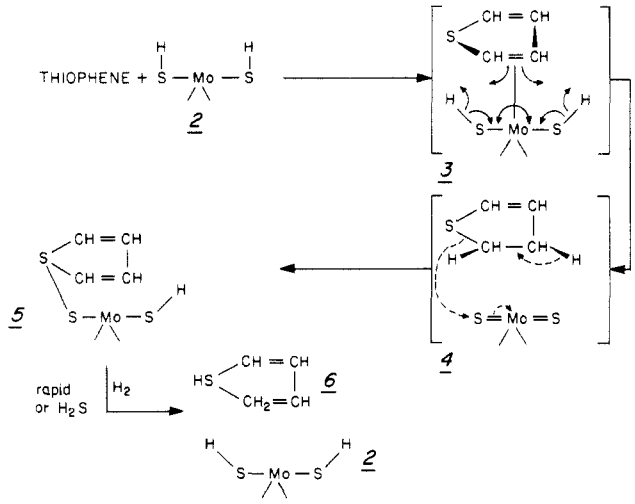

Figure 2. Multipoint adsorption reaction mechanism for hydrogenation on a sulfided molybdena catalyst with resultant β elimination and hydrogenolysis.

TABLE I: Experimental Conditions

reactor	300-cm^3 autoclave operated in the batch mode, stirring speed 1700 rpm
catalyst	Co-Mo/γ-Al_2O_3 (American Cyanamid HDS-16A; 3.5 wt % CoO, 18 wt % MoO_3), 150-200 mesh, presulfided for 2 h at 673 K in 200 cm^3/min of 10% H_2S in H_2 to give a 10-fold excess of sulfur; transfer done to exclude air
temperature	573 ± 2 K
pressure	6.89 × 10^6 Pa (68 atm)
catalyst loading	~0.5 wt % of total reaction mixture
carrier oil	150.2 g of *n*-hexadecane
reactant concn	0.25 mol % (0.22 wt %) phenothiazine in *n*-hexadecane; or 0.25 mol % (0.20 wt %) dibenzothiophene and 0.25 mol % (0.20 wt %) acridine in *n*-hexadecane

the autoclave which allowed a slurry of catalyst and reactant(s) mixed with *n*-hexadecane carrier oil to be injected into the autoclave which contained the remainder of the *n*-hexadecane and which had been stabilized at reaction conditions. This procedure prevented the problems of reaction occurring or of the catalyst changing during long heat-up times and gave a uniquely defined zero time for the reaction, allowing quantitative kinetic studies to be done. Standard operating conditions for these studies are summarized in Table I. The catalyst was presulfided, and sufficient H_2S was maintained in the H_2 in the autoclave to maintain the catalyst in the fully sulfided state.

At zero time the catalyst and reactants were injected into the autoclave with H_2 at the desired pressure. Liquid samples were removed from the autoclave periodically for analysis to follow the course of the reaction. Reaction products were analyzed by gas chromatography (Perkin-

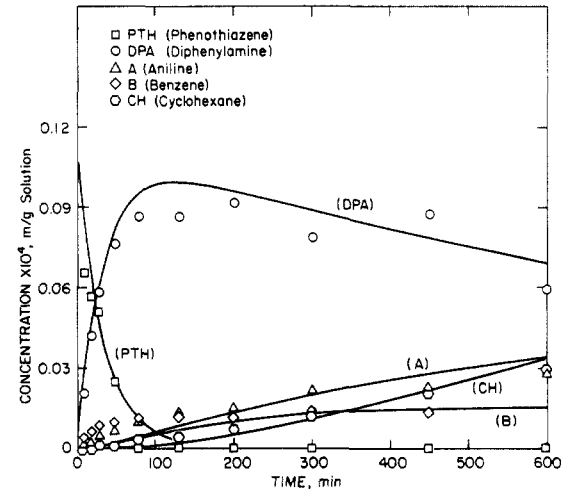

Figure 3. Product distribution vs. time for catalytic hydroprocessing of phenothiazine catalyzed by sulfided Co-Mo/γ-Al_2O_3 at 573 K and 68 atm. The curves drawn are computer simulated, based on the network and pseudo-first-order rate parameters of model II.

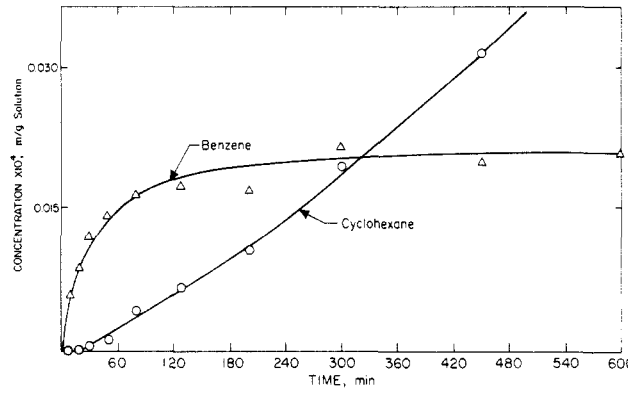

Figure 4. Behavior of benzene and cyclohexane in phenothiazine reaction catalyzed by sulfided Co-Mo/γ-Al_2O_3. Reaction conditions given in Table I.

Elmer Model 3920) using a flame ionization detector (FID) and a nitrogen-specific detector. A 0.8 mm o.d. × 0.025 mm i.d. × 100 m wall-coated open tubular column with an OV-101 liquid phase and maintained at 463 K was used.

Results

Analysis of the liquid samples from the phenothiazine reaction using the nitrogen-specific detector showed that only three nitrogen-containing species were present in liquid samples taken periodically over a 10-h reaction period; they were phenothiazine, diphenylamine, and aniline. No organic sulfur-containing products were observed. The concentration vs. time behavior of the nitrogen-containing and hydrocarbon species is shown in Figure 3. The parent compound (1) concentration decreases continually with time. The diphenylamine concentration rises from zero at the start of reaction to a maximum value, at which time all phenothiazine has been reacted. The concentration of diphenylamine then steadily decreases. Aniline concentrations were relatively low throughout the experiment but are also seen to rise from zero at the start of reaction to a maximum value and then begin to decrease. The behavior is that of a classical consecutive reaction network:

$$A \rightarrow B \rightarrow C \rightarrow D$$

Solid curves in Figure 3 are a computer simultation based on pseudo-first-order kinetics and the reaction network discussed below.

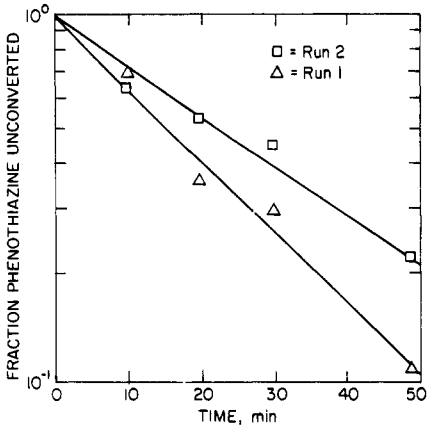

Figure 5. Semilog plot for phenothiazine hydrodesulfurization catalyzed by sulfided Co–Mo/γ-Al_2O_3 illustrating pseudo-first-order kinetic behavior. Reaction conditions given in Table I, the weight of catalyst/weight of carrier oil ratio was different for each run. Run 1: 0.216 g of catalyst, k = 31 ± 4 g of oil/(g of catalyst·min). Run 2: 0.1760 g of catalyst, k = 26 ± 6 g of oil/(g of catalyst·min).

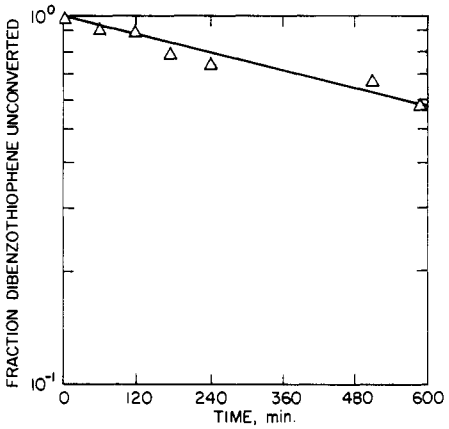

Figure 6. Hydrodesulfurization of dibenzothiophene in the presence of acridine catalyzed by sulfided Co–Mo/γ-Al_2O_3 pseudo-first-order kinetic behavior illustrated. Reaction conditions given in Table I. k = 0.64 ± 0.06 g of oil/(g of catalyst·min).

The concentrations of benzene and cyclohexane formed were monitored carefully from the very beginning of reaction. Typical results, which are depicted in Figure 4, reveal that the benzene concentration initially rises much faster than that of cyclohexane but ultimately reaches a maximum value and even shows a slight decrease suggesting that benzene not only is being formed but is also undergoing hydrogenation. The cyclohexane concentration, which begins with an essentially zero slope, increases rapidly at longer reaction times. Similar behavior has previously been observed in the HDN reactions of diphenylamine, of aniline, and of ethylaniline.[4] These results have been interpreted in terms of a multipoint reaction mechanism for the HDN reactions, which is similar to that depicted in Figure 2 for the HDS reaction. This mechanism involves an initial hydrogenation of the aromatic ring, followed by a β-elimination reaction which restores the benzenoid structure of the ring to the product which desorbs.

A repeat run was performed under the same reaction conditions to check the reproducibility of the results obtained and also to more clearly define the product vs. time behavior for the phenothiazine reaction catalyzed by sulfided Co–Mo/γ-Al_2O_3. The results of the combined nitrogen-specific and FID analyses of liquid reaction mixture samples obtained over a 10-h period are the same as shown in Figures 3 and 4, indicating a very high degree of reproducibility. Again, no sulfur-containing organic compounds other than the parent compound were detected in any of the product samples.

Results obtained by other investigators[5-10] have shown that both HDS and HDN reactions, similar to the phenothiazine reaction presented here, may be characterized by pseudo-first-order kinetics for conditions of constant temperature and H_2 concentration. For reaction conditions identical with those used here, Nag[10] estimated the concentration of H_2 in the reaction mixture to be 13 mol%. Thus, the initial molar ratio of H_2 to organic reactant was approximately 50. Under these conditions, the concentration of H_2 may be taken to be constant. Figure 5 demonstrates the applicability of pseudo-first-order kinetics for the hydroprocessing of phenothiazine; within experimental error linear behavior is observed. The straight lines drawn through the data in Figure 5 do not coincide because a different amount of catalyst was used for each run. Standard linear regressions of the data in Figure 5 taking into account the different amounts of catalyst gave the following pseudo-first-order rate constants for HDS of phenothiazine: run 1, k = 31 ± 4 g of oil/(g of catalyst·min); run 2, k = 26 ± 6 g of oil/(g of catalyst·min). These two rate constants are for 95% confidence limits; they show that the reproducibility of the phenothiazine hydrodesulfurization reaction was good.

Further data were taken to allow a direct comparison to be made between the rate of phenothiazine hydrogesulfurization and that of dibenzothiophene hydrodesulfurization and to estimate the extent of inhibition of such nitrogen-containing species on the primary hydrodesulfurization reaction of phenothiazine. In these studies an equimolar mixture of dibenzothiophene and acridine was used as a reasonable facsimile of the inhibition caused by the assumedly independently acting sulfur and nitrogen functionalities of the phenothiazine molecule. The mixture contained an amount of nitrogen on a molar basis equal to what was present in the phenothiazine runs. It was expected that the acridine would depress the rate of dibenzothiophene hydrodesulfurization since the basic nitrogen on acridine would absorb strongly on active hydrodesulfurization catalyst sites. The analysis in this case was focused only on determining the concentration–time behavior of dibenzothiophene and of its hydrodesulfurization products. Analysis of samples taken periodically over a 10-h reaction period showed only dibenzothiophene and biphenyl as the relevant components of the mixture. The dibenzothiophene concentration decreased slowly with a corresponding increase in the biphenyl concentration; no cyclohexylbenzene or bicyclohexyl were observed. Other investigators[9,10] identified cyclohexylbenzene and bicyclohexyl as hydrodesulfurization products of dibenzothiophene. The absence of these products in the dibenzothiophene–acridine run is reasonable since the acridine molecule will compete with biphenyl for active hydrogenation sites.[6,7] This should

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significantly retard the rate of hydrogenation of biphenyl.

The applicability of pseudo-first-order kinetics for this reaction is illustrated in Figure 6. The pseudo-first-order rate constant obtained by a linear regression of the data (95% confidence limits) for dibenzothiophene hydrodesulfurization ($k = 0.64 \pm 0.06$ g of oil/(g of catalyst·min) in the presence of acridine is about 50-fold lower than the rate of hydrodesulfurization of phenothiazine at the same reaction conditions (k = 26–31 g of oil/(g of catalyst·min)).

Discussion

We will first consider the overall reaction network involved in the hydroprocessing of phenothiazine and then consider the mechanism of hydrodesulfurization. Figure 3 shows that diphenylamine is the primary product formed from phenothiazine, resulting from removal of sulfur as H_2S. The next reaction in the network involves C–N bond scission leading to aniline plus benzene. We have recently shown that this type of deamination reaction involves partial hydrogenation of the aromatic ring followed by β elimination leading to the aromatic ring and the eliminated amine.[4] The aniline then undergoes the same type of partial hydrogenation followed by β elimination leading to NH_3 and benzene. The benzene is hydrogenated to cyclohexane as shown in Figure 4.

As was previously demonstrated, the reactants and intermediates of the HDN process are all converted in reactions which follow pseudo-first-order kinetics. The data were fitted to a consecutive reaction network using a set of pseudo-first-order reactions of the form

$$-(M_o/M_c)(dC_i/dt) = -k_{ij}C_i$$

where M_o = mass of the carrier oil in grams, M_c = mass of the catalyst in grams, C_i = the concentration of species i (gram moles of i per gram of oil), t = time (minutes), k_{ij} = pseudo-first-order rate constant for species i in the jth reaction (g of oil/(g of catalyst·min)). The rate equations were then solved by using the Marquardt method.[11] This method minimizes the weighted residual sum of the squares of all responses.

When the Marquardt algorithm was applied to a series of reaction networks, only two chemically feasible networks yielded all positive rate constants; the others were disqualified. Using the symbols phenothiazine = PTH, diphenylamine = DPA, aniline = A, benzene = B, and cyclohexane = CH, the two qualifying networks were

model I

$$\mathrm{PTH} \xrightarrow{k_1} \mathrm{DPA} \xrightarrow{k_2} \mathrm{B} + \mathrm{A} \xrightarrow{k_3} \mathrm{B} \underset{k_5}{\overset{k_4}{\rightleftharpoons}} \mathrm{CH}$$

model II

$$\mathrm{PTH} \xrightarrow{k_1} \mathrm{DPA} \xrightarrow{k_2} \mathrm{B} + \mathrm{A} \xrightarrow{k_3} \mathrm{B} \xrightarrow{k_4} \mathrm{CH}$$

Though both models reproduced the experimental data very satisfactorily (Figure 3) (and model I must ultimately be true), model I was eliminated from further consideration because the calculated equilibrium constant, $k_4/k_5 = K_4$, was >2500, whereas the actual value for the equilibrium $B + 3H_2 \rightleftarrows CH$ is of the order of 20–30. This shows that, for the extent of reaction (reaction time) studied, the reverse reaction (CH → B) was not yet sufficiently important to be elucidated kinetically. The rate parameters computed for model II are at the 95% confidence level. They are listed in Table II.

The value of k_1 is in excellent agreement with the values obtained from the semilog plot (Figure 5). The values of the pseudo-first-order rate constants for the hydrodenitrogenation reactions are about 40-fold lower than that for the hydrodesulfurization reaction. This clearly illustrates how much more difficult C–N bond scission (HDN) is than C–S bond scission (HDS). Further, the pseudo-first-order rate constant for C–N bond scission in diphenylamine (0.71 min^{-1}) is essentially the same as that for C–N bond scission in aniline (0.58 min^{-1}), consistent with our observation that the reaction mechanism is the same for all aniline species.[4] The pseudo-first-order rate constant for dibenzothiophene hydrodesulfurization catalyzed by sulfided Co–Mo/γ-Al_2O_3 at 71 atm and 573 K is 28 g of oil/of catalyst·min)[10] in the absence of any nitrogen-containing compounds; this is in extremely good agreement with that observed here for hydrodesulfurization of phenothiazine (Table II, Figure 5). Benzene hydrogenation and biphenyl hydrogenation have been shown to be slower than the hydrodesulfurization of dibenzothiophene[12] catalyzed by sulfided Co–Mo/γ-Al_2O_3, as observed here (Table II).

TABLE II: Rate Parameters[a] Determined for Reaction Network II

rate parameter	run 1[a]	rate parameter	run 1[a]
k_1 (PTH → DPA)	24.7	k_3 (A → B)	0.58
k_2 (DPA → B + A)	0.71	k_4 (B → CH)	4.4

[a] In units of g of oil/(g of catalyst·min) determined by the Marquardt method.[11]

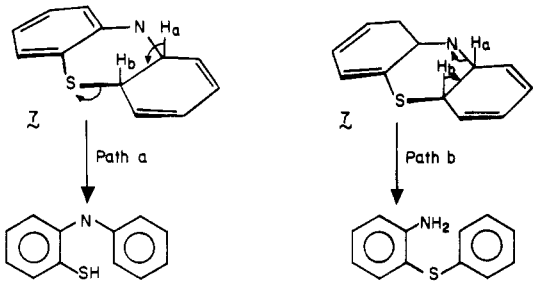
Comparison of the pseudo-first-order rate constants for hydrodesulfurization of phenothiazine, $k_1 \simeq$ 25–31 g of oil/(g of catalyst·min), with that for the hydrodesulfurization of dibenzothiophene, $k \simeq$ 28 g of oil/(g of catalyst·min), under comparable reaction conditions but in the absence of any nitrogen-containing compounds, is very informative. The one-point adsorption reaction mechanism (Figure 1) would very strongly suggest that the rate of hydrodesulfurization of phenothiazine should be less than that of dibenzothiophene due to the adsorption competition between the nucleophilic nitrogen and the sulfur in phenothiazine for active sites on the catalyst. That is to say, the one-point adsorption reaction mechanism for hydrodesulfurization of phenothiazine would have to involve inhibition of the hydrodesulfurization rate both by the nitrogen center in phenothiazine and in the nitrogen-containing products formed in the hydrodesulfurization reaction of phenothiazine, namely, the diphenylamine and ultimately the aniline. Because of the observed strong inhibition of the hydrodesulfurization reaction rate by nitrogen-containing compounds,[6,7] the phenothiazine hydrodesulfurization rate would be expected to be lower than that of dibenzothiophene alone; just the opposite was observed.

In order to gain a rough estimate of the inhibitory effects of such nitrogen-containing species on the primary hydrodesulfurization reaction of phenothiazine, the equimolar mixture of dibenzothiophene and acridine was taken to represent the (assumedly) independently acting sulfur and nitrogen functionalities of phenothiazine. The experimental data show an approximately 40-fold decrease in the rate of hydrodesulfurization of dibenzothiophene in the presence of acridine (k_1 = 0.64 g of oil/(g of catalyst·min), compared to $k_1 \simeq$ 28 g of oil/(g of catalyst·min) in the absence of acridine). The overall rate of hydrodesulfurization of dibenzothiophene under these conditions, chosen to represent the phenothiazine reaction conditions, is also 40-fold lower than the rate of phenothiazine hydrodesulfurization, $k_1 \simeq$ 25 g of oil/(g of cat-

(11) Marquardt, D. W. *J. Soc. Ind. Appl. Math.* **1963**, *11*, 431.

(12) Sapre, A. V.; Gates, B. C. *Ind. Eng. Chem. Process. Des. Dev.*, in press.

Scheme I



alyst·s).

The most attractive explanation, therefore, of the exalted rate of hydrodesulfurization of phenothiazine is that the applicable hydrodesulfurization mechanism involves flat, multipoint, or ring adsorption on the catalyst surface in such a manner that the nitrogen atom is strongly involved and strongly facilitates the adsorption. This also suggests that an initial hydrogenation of the benzenoid ring is involved in the reaction mechanism. The greater π-electron availability on the benzene rings of phenothiazine obtained by way of the associated nitrogen atom compared to dibenzothiophene most probably accounts for the exalted rate of the hydrogenation step and of the hydrodesulfurization step. The preference for breaking the C–S rather than the C–N bond in the subsequent reaction steps requires further consideration of the reaction process in which β elimination is completed from the intermediate dihydrophenothiazine, **7** (see Scheme I).

If the β-elimination step merely involved removal of a proton (by an as yet unidentified acceptor), the choice between path a and path b is unequivocal. Other than H_2S, no sulfur-containing reaction products were ever observed, suggesting that, once the aromatic thiol was formed, it underwent rapid hydrodesulfurization eliminating H_2S. While removal of H_a is favored by the greater electronegativity of nitrogen, the loss of the H_b proton (resulting in C–N bond rupture) is even more favored by the much greater stability of an α-thiocarbanion;[13] i.e., the sulfur yields driving force far exceeds that of the nitrogen ylid. However, since the C–S bond is the one which is broken, we conclude that the driving force for the overall process is related instead to the considerably lower bond strength of the C–S (~272 kJ/mol) vs.the C–N covalency (~305 kJ/mol). Since this is the case, if we are to develop better catalysts, we must seek to identify and develop catalytic sites that are more active in this partial hydrogenation and that can take advantage of the relative weakness of the C–S bond.

Such considerations suggest the following modification (Figure 7) of the previously proposed hydrodesulfurization reaction mechanism. Therein, the proposed C–S bond hydrogenolysis reaction site (**2a** in Figure 7) possessing an anion vacancy on molybdenum[1,3,14,15] is directly implicated in the β-elimination step. This assignment is made on the basis of the reactivity of certain transition elements at this valence level in undergoing a 1,1 addition (sometimes called 1,1 insertion or oxidative addition[16]) with relatively weak carbon covalencies. Figure 7 shows not only that this

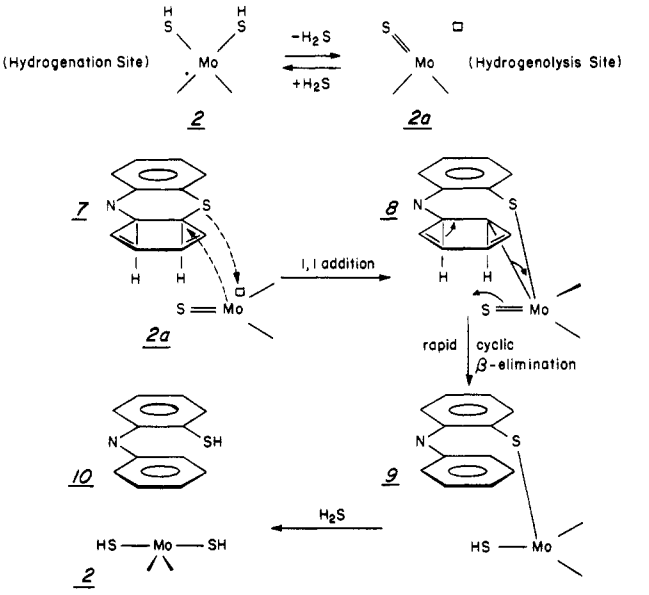


Figure 7. Proposed catalyst-assisted hydrogenolysis mechanism for hydrodesulfurization of phenothiazine.

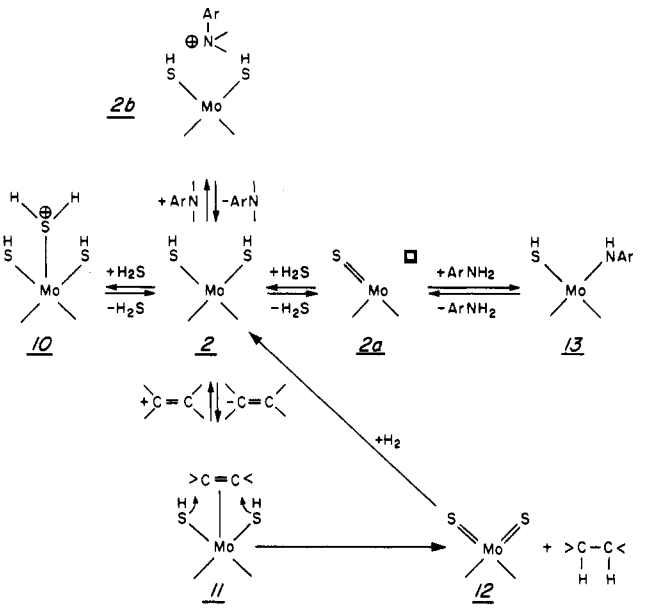


Figure 8. Proposed hydrogenation pathways and the role of H_2S.

1,1-addition complex could be formed faster in the case of a weak C–S covalency (vs. a stronger C–N covalency) but that it also could lead to an alkyl–transition element complex, **8**, which is known[17] to readily undergo a subsequent cyclic β-elimination process. This step is particularly rapid when driven by the concomitant rearomatization to the (diphenylamine) rings in **9** and **10**.

The alternative reaction path (path b in Scheme I) which would result in C–N bond hydrogenolysis is probably the slow step in reaction catalyzed by the sulfided Co–Mo/γ-Al_2O_3. In fact, the oxidative addition to the C–N bond is so much slower that, in most cases, full hydrogenation of the aromatic ring is completed in large measure before any hydrogenolysis through oxidative addition can be observed to take place.[5-8,18] By comparison, hydrogenated intermediates containing sulfur are present only in low concentrations during the course of the hydrodesulfurization of dibenzothiophene.[9,10] No hydrogenated sulfur-con-

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(15) Okamoto, Y.; Tomiaka, H.; Imanaka, T.; Teranishi, S. *J. Catal.* **1980**, *66*, 93.

(16) See: Purcell, K. F.; Kotz, J. C. "Inorganic Chemistry"; W. B. Sanders: Philadelphia, PA, 1977; pp 947 et seq. for discussion of the mechanism of this process.

(17) See ref 16, pp 948 et seq.

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taining compounds were observed here.

On the basis of the proposed model of catalytic sites,[3,14,15] we infer that a given catalytic site is potentially capable of catalyzing both the hydrogenation and hydrogenolysis reactions in ratios that depend upon the extent of interconversion of the two structures, **2** and **2a** in Figure 7, and are both inhibited by adsorption of H_2S and aromatic amines as shown in Figure 8. Hydrogenation sites may be directly removed from operation by adsorption of a basic amine as shown in **2b** in Figure 8. Hydrogenolysis is inhibited when the anionic vacancy of a hydrogenolysis site (**2a**) is vitiated through coordination of the latter with an (unreduced) aromatic amine inhibitor (**13**, Figure 8). This can be seen to account for the inhibitory effects of aromatic nitrogen on both the hydrogenation and the overall hydrodesulfurization and hydrodenitrogenation reactions of the catalyst. The potential inhibitory effect of H_2S on hydrogenation can be attributed to formation of a multicoordinate complex **10** in which H_2S becomes a ligand of the hydrogenation site **2** (see also a +6 molybdenum in Figure 1). In much the same manner, a >C=C< π bond is complex coordinated, before its reduction, as depicted in **11** → **12** in Figure 8.

A recent article[19] describing inhibition by various amines under mild hydrodesulfurization conditions reports that aromatic nitrogen heterocycles containing alkyl substituents which strongly shield the lone pair *do not inhibit the HDS reaction under catalytic conditions which minimize hydrogenation activity*. This very interesting observation suggests that the sp^2 lone pair on (for example) a pyridine nitrogen is normally responsible for inhibition of HDS through coordination of the anionic vacancy in **2a** as discussed above. Alkyl substituents in these cases apparently obstruct such coordination at **2a** and thus 2,6-dimethylpyridine (for example) is found[18] to be ineffective as an HDS inhibitor. Coordination of the sp^2 unshared pair in pyridine which projects from the plane of the ring is thus seen to result in an end-on configuration of the ring relative to the active center. It is thus configuration which cannot be achieved when sterically hindering alkyl groups are present.

However, it must be recognized that 2,6-dimethylpyridine is readily hydrogenated *under ordinary conditions*, indicating that the hydrogenation site **2** easily binds the π electron cloud projecting perpendicular to the ring and holds the ring in the planar configuration necessary for the ensuing cis-hydrogen addition step. The resulting 2,6-dimethylpiperidine is indeed an effective inhibitor of the HDS reaction because the sp^3 lone pair in the *puckered* structure is *not* completely obstructed by the 2,6 alkyl substituents. Moreover, we would expect that, subsequent to coordination of this piperidine, the hydrodenitrogenation reaction steps would proceed as found for other aliphatic amines (e.g., benzylamine) by Gutberlet and Bertolacini.[19]

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Vacuum-Ultraviolet Photolysis of Methylamine†

Edward P. Gardner‡ and James R. McNesby*

Department of Chemistry, University of Maryland, College Park, Maryland 20742 *(Received: September 1, 1981; In Final Form: February 2, 1982)*

Photolyses of methylamine have been carried out at 184.9, 147.0 and 123.6 nm. Quantum yields of hydrogen, hydrocarbons, and nitrogen have been measured. Evidence has also been obtained for the formation of HCN and CN in primary processes at the shorter wavelengths. Photolyses of CD_3NH_2 in the presence of oxygen and NO provide evidence that H and D atom production dominates at 184.9 nm while H_2 and D_2 elimination occurs to an important extent at 147.0 and 123.6 nm. The primary process of molecular hydrogen elimination is partly terminal and partly nonterminal.

Introduction

The synthesis of organic compounds (e.g., HCN and H_2CO) by electric discharges in mixtures of methane, ammonia, and water was first achieved in the laboratory by Miller.[1,2] Among the compounds produced were several of biological interest causing, in the mid-1950s, a revival of interest in prebiotic chemistry[3,4] to explain the origin of simple life forms. These early experiments spawned a series of successful efforts to produce similar results using ultraviolet light as the energy source.[5-16] It was not until 1979, however, that the molecule responsible for the establishment of the C–N bond in photolysis of CH_4/NH_3 mixtures was identified experimentally as methylamine.[17,18] This observation has been confirmed by Bossard and Toupance.[19] The photochemistry of methylamine has, therefore, assumed new relevance to prebiotic photochemical synthesis.

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‡ Department of Planetary Science, California Institute of Technology, Pasadena, CA 91125.

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