

# Selectivity of Molybdenum Catalyst in Hydrodenitrogenation, Hydrodesulfurization, and Hydrodeoxygenation: Effects of Sulfur and Oxygen Compounds on Acridine Hydrodenitrogenation

MASATOSHI NAGAI, TAKASHI MASUNAGA, AND NOBUAKI HANA-OKA

*Department of Chemical Engineering, Tokyo University of Agriculture and Technology,  
Koganei City, Tokyo 184, Japan*

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The selectivity of a Mo/Al<sub>2</sub>O<sub>3</sub> catalyst in denitrogenation, desulfurization, and deoxygenation based on the retarding effect of sulfur and oxygen compounds on acridine hydrodenitrogenation has been studied. The experiments were done in a continuous flow microreactor at 280–380°C and 10.1 MPa total pressure. Sulfidation of the reduced catalyst hindered the denitrogenation of perhydroacridine to dicyclohexylmethane. The sulfur and oxygen compounds, except for a small amount of CS<sub>2</sub>, depressed the denitrogenation at higher temperatures where the intermediate hydrogenations of acridine to perhydroacridine attained equilibria. At lower temperatures, all the additives affected the hydrogenation of octahydroacridine to perhydroacridine which was not at equilibrium and resulted in a decrease of denitrogenation. The kinetics and reaction mechanism of the retarding effects are also discussed. © 1986 Academic Press, Inc.

## INTRODUCTION

Hydrodenitrogenation will become increasingly important in the future for lowering the nitrogen content of low-grade petroleum feedstocks, synthetic crudes extracted from oil shale, and coal-derived liquids. There are many articles on the hydrodenitrogenation of simple model compounds, such as quinoline (1–3), benzoquinoline (4), acridine (2, 5), and carbazole (6), which are found in heavy feedstocks. In a practical process, however, hydrodenitrogenation occurs simultaneously with hydrodesulfurization, and therefore an understanding is required of the influence of one reaction upon the other and what kind of catalyst sites are active in both reactions or separately.

There are several studies on the effects of nitrogen compounds on hydrodesulfurization. Nitrogen compounds greatly decreased the conversion of thiophene (7, 8) and benzothiophene (9) on sulfided Mo/Al<sub>2</sub>O<sub>3</sub> and CoMo/Al<sub>2</sub>O<sub>3</sub> catalysts. Our recent studies of the poisoning effects of ni-

trogen compounds found that the decrease in the conversion of dibenzothiophene hydrodesulfurization was due to inhibition of dibenzothiophene hydrogenation by the strong adsorption of nitrogen compounds (10) and that the poisoning effect was related to their gas phase basicities (11).

On the other hand, a few studies have been performed determining the effects of sulfur compounds on the hydrodenitrogenation of pyridine (12) and quinoline (13–16). Studies on the effects of H<sub>2</sub>S (generated by CS<sub>2</sub>) on quinoline hydrodenitrogenation suggested that the presence of H<sub>2</sub>S remarkably enhanced the hydrogenolysis of tetrahydroquinoline to *o*-propylaniline (13, 14) but inhibited the intermediate hydrogenation steps (13–15) and the denitrogenation of *o*-propylaniline (15). In addition, a study of the competitive reaction of pyridine and thiophene yielded the same observation as that of the H<sub>2</sub>S effect on quinoline hydrodenitrogenation (12).

A number of questions remain to be answered about the following problems: (1)

To what extent does sulfidation of the catalyst influence the hydrodenitrogenation? (2) Is a good mass balance maintained before and after addition? (3) Since a little  $\text{CS}_2$  enhances the condensation of hydroquinolines (16), is hydrodenitrogenation enhanced by other sulfur compounds as well as  $\text{H}_2\text{S}$ ? (4) Are similar results obtained even for the reaction of different types of nitrogen compounds such as a  $\pi$ -deficient or  $\pi$ -excessive ones?

In this study, we choose acridine as the model compound of a  $\pi$ -deficient three-ring nitrogen compound. It is similar to the heterocyclic nitrogen compounds, pyridine and quinoline. Furthermore, since there is little knowledge of the effect of oxygen compounds on hydrodenitrogenation, xanthene was chosen as a three-ring oxygen compound.

In this study, we determined the effect of sulfiding a  $\text{Mo}/\text{Al}_2\text{O}_3$  catalyst and the kinetics of the retarding effect of sulfur and oxygen compounds on the hydrodenitrogenation of acridine on a  $\text{Mo}/\text{Al}_2\text{O}_3$  catalyst. The mechanism of the hydrodenitrogenation on a  $\text{Mo}/\text{Al}_2\text{O}_3$  catalyst and the selectivity of the catalyst in denitrogenation, desulfurization, and deoxygenation are also discussed.

## EXPERIMENTAL

**Catalyst and reagents.** The catalyst, 12.5 wt%  $\text{MoO}_3$  on  $\gamma\text{-Al}_2\text{O}_3$ , has been previously used (9). Catalyst granules between 0.84 and 1.19 mm were used.  $\text{H}_2\text{S}$  (To-ei Chemical Co., 99.9%) was used without purification. Hydrogen (To-ei Chemical Co., 99.9%) was dried by passing it through a Linde 13X molecular sieve trap prior to use. Dibenzothiophene was synthesized according to Gilman and Jacoby (17) and was purified using ethanol. Acridine (Tokyo Kasei Kogyo Co., Ultra Pure Grade) and all other reagents (Extra Pure Grade) were used without purification.

**Apparatus and procedure.** The continuous flow microreactor consisted of an 11-

mm-i.d. stainless steel tube, in a vertical configuration. The fresh catalyst (2.0 g) was first heated in air for more than 24 h at  $450^\circ\text{C}$  in the reactor. Reduction was carried out *in situ* by exposing the oxidized catalyst to hydrogen at  $400^\circ\text{C}$  and 10.1 MPa pressure for 4 h. Sulfiding was accomplished with a 10%  $\text{H}_2\text{S}/\text{H}_2$  mixture flowing at 30 liters/h at atmospheric pressure and  $400^\circ\text{C}$  for 3 h after reduction.

After either reduction or sulfidation the reactor was cooled to a desired temperature with a  $\text{H}_2$  (or  $\text{H}_2\text{S}/\text{H}_2$ ) stream and then a solution containing 0.25 wt% acridine in xylene was allowed to flow into the reactor. After about 3 h the reaction reached a steady state. The solution was then replaced by another solution containing both acridine and an additive compound. The next feed containing acridine and a more concentrated compound than the previous one was then replaced after 2 h. For the temperature dependence experiment determining product distribution with a sulfided catalyst, the solution contained about 0.003 wt% ethanethiol as well as acridine in order to maintain the sulfide state of the catalyst. No sign of deactivation of the catalyst was observed during the 13 h run.

**Analytical.** After the reaction, the liquid products were analyzed by gas chromatography with a flame ionization detector. The column was a 2-m-long, 3-mm-i.d. glass column packed with 2% Dexsil 400 GC on 60–80 mesh Uniport HP. Temperatures ranged from 80 to  $200^\circ\text{C}$ . Gaseous products, such as  $\text{H}_2\text{S}$  and any light cracking products, could not be determined because of their dilution.

The main products, which were 9,10-dihydroacridine, *cis*- and *trans*-1,2,3,4,4a,9,9a,10-octahydroacridine,  $\alpha$ -perhydroacridine, and dicyclohexylmethane, were isolated with a gas chromatograph equipped with a T.C.D. detector and were identified by the data obtained from melting point, IR (Nihon Bunko), high-resolution mass spectrometry (Hitachi, RMU-7M), and NMR (Nihon Denshi, JNM-FX 100)

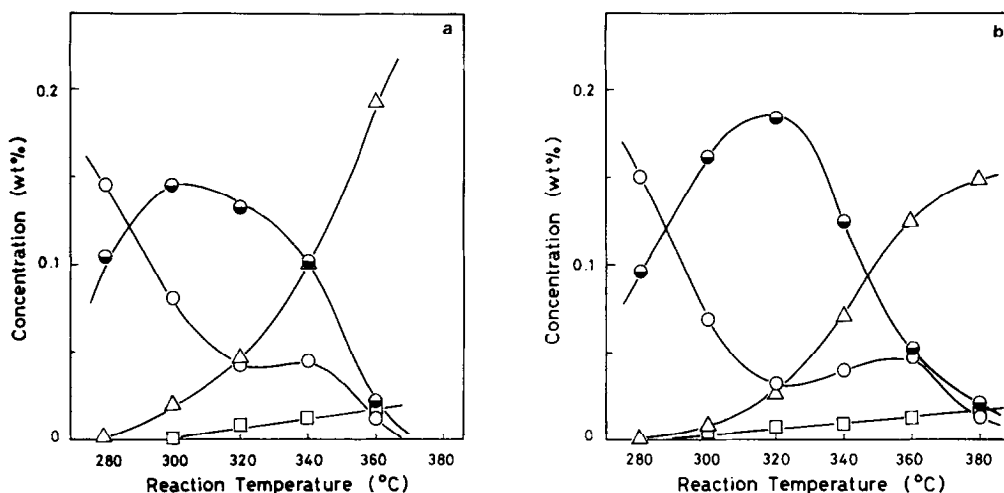


FIG. 1. Change in product composition of acridine hydrogenation on the reduced (a) and sulfided (b)  $\text{Mo}/\text{Al}_2\text{O}_3$  catalyst as a function of temperature. Reaction conditions: 10.1 MPa total pressure, 0.25 wt% of acridine, 500 ml (STP)  $\text{H}_2$ /mole, 20 ml/h of feed solution. Reaction products:  $\circ$ , octahydroacridine;  $\bullet$ , perhydroacridine;  $\square$ , benzylcyclohexylhexane;  $\Delta$ , dicyclohexylmethane.

(5). Benzylcyclohexylhexane was analyzed by mass spectral analysis using a GC-MS (Shimadzu, LK 9000).

## RESULTS

### Sulfidation of the $\text{Mo}/\text{Al}_2\text{O}_3$ Catalyst

The changes in the product distribution of acridine hydrogenation on the reduced and sulfided  $\text{Mo}/\text{Al}_2\text{O}_3$  catalyst at 10.1 MPa total pressure are shown in Figs. 1a and b. Acridine was hydrogenated to 9,10-dihydroacridine very rapidly even at 280°C. Dihydroacridine was hydrogenated successively to octahydroacridine and perhydroacridine, which were then denitrated above 300°C to benzylcyclohexyl-

hexane and dicyclohexylmethane, respectively. At 340°C, the major reaction products were perhydroacridine and dicyclohexylmethane, with negligible concentrations of acridine and dihydroacridine. The product distribution with the sulfided catalyst was similar to that with the reduced catalyst. The hydrogenation of acridine on both catalysts apparently proceeded via the reaction pathway (5) shown in Fig. 2.

During sulfidation of the reduced catalyst, more of the hydrogenated acridine compounds were produced as compared to those on the reduced catalyst in the range of 280 to 340°C, but the dicyclohexylmethane concentration dropped by 50% at all

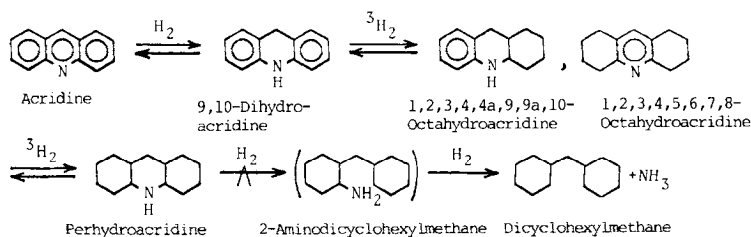


FIG. 2. Reaction scheme for the hydrogenation of acridine.

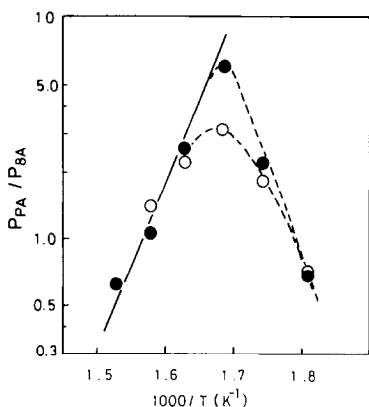


FIG. 3. Estimation of the equilibrium constant for the hydrogenation of octahydroacridine (8A) to perhydroacridine (PA) on the reduced (○) and sulfided (●) catalyst.

reaction temperatures. It implied that sulfidation decreased the activity of the Mo/Al<sub>2</sub>O<sub>3</sub> catalyst during the formation of the dicyclohexylmethane from perhydroacridine. The apparent activation energies for the formation of dicyclohexylmethane on the reduced and sulfided catalysts were 135 and 156 kJ/mole, respectively.

#### *Equilibria among Acridine and the Reaction Products during Hydrodenitrogenation*

The equilibrium analysis for acridine hydrodenitrogenation by Cocchetto and Satterfield (18) could not be compared with our experimental results because their data were based on the direct denitrogenation of acridine to diphenylmethane. The estimation of the equilibrium by the Krevlen group contribution technique was not done because the values were inaccurate. Hence, the equilibrium constants were estimated for the reaction steps during hydrogenation using the ratio of the reaction products. The molar ratio of perhydroacridine to octahydroacridine is shown in Fig. 3. The ratio for the reduced catalyst increased to 340°C and then decreased with increasing temperature. Therefore, equilibrium of the hydrogenation appeared to be attained at 340°C. In addition, equilibrium

of the hydrogenation reaction was attained more rapidly with the sulfided catalyst than with the reduced catalyst. Equilibrium was approached at 320°C. It is apparent that acridine and dihydroacridine are completely converted to octahydroacridine even below 280°C, as shown in Fig. 1. Although the amounts of both acridine and dihydroacridine are negligible at higher temperatures and their molar ratio is unable to be calculated, the hydrogenations of acridine to octahydroacridine seem to approach equilibria. Hence, the hydrogenation of acridine to perhydroacridine on the reduced and sulfided catalyst appears to be in equilibrium above 340 and 320°C, respectively, with the denitrogenation of perhydroacridine to dicyclohexylmethane the rate-determining step.

#### *Effect of Sulfur Compounds on Acridine Hydrodenitrogenation*

The change in the product composition of acridine hydrodenitrogenation on the reduced catalyst in the presence of thiophene at 360°C is shown in Fig. 4. The mass bal-

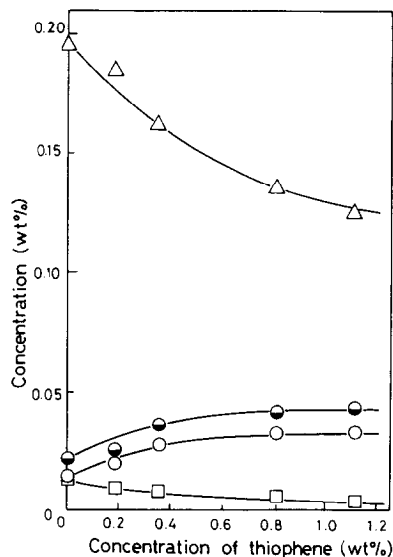


FIG. 4. Effect of thiophene on the products of acridine hydrodenitrogenation on the reduced catalyst at 360°C. Δ, Dicyclohexylmethane; ●, perhydroacridine; ○, octahydroacridine; □, benzylcyclohexylhexane.

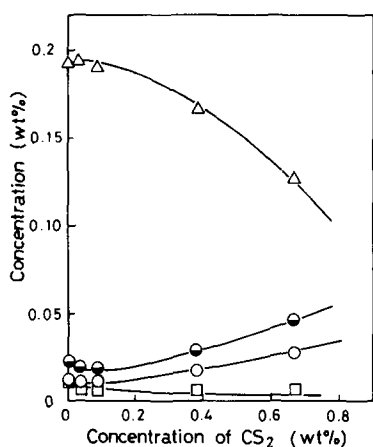


FIG. 5. Effect of  $\text{CS}_2$  on the products of acridine hydrodenitrogenation on the reduced catalyst at  $360^\circ\text{C}$ .  $\Delta$ , Dicyclohexylmethane;  $\bullet$ , perhydroacridine;  $\circ$ , octahydroacridine;  $\square$ , benzylcyclohexylhexane.

ance is maintained at more than 90% before and after addition. However, the mass balance on the addition of  $\text{CS}_2$  at  $360^\circ\text{C}$  in Fig. 5 is slightly lower than that during the addition of the other sulfur compounds. Addition of thiophene decreased the dicyclohexylmethane concentration with increasing concentrations of octahydroacridine and perhydroacridine. Similar observations were made during the experiments using either the other sulfur compounds (Fig. 5) or the sulfided catalyst at  $360^\circ\text{C}$

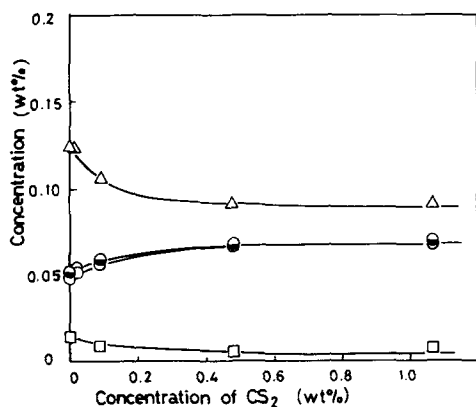


FIG. 6. Effect of  $\text{CS}_2$  on the products of acridine hydrodenitrogenation on the sulfided catalyst at  $360^\circ\text{C}$ .  $\Delta$ , Dicyclohexylmethane;  $\bullet$ , perhydroacridine;  $\circ$ , octahydroacridine;  $\square$ , benzylcyclohexylhexane.

(Fig. 6). The formation of dicyclohexylmethane (moles) decreased in the following sequence: dibenzothiophene > benzothiophene > dimethyl sulfide > thiophene > ethanethiol. This indicates that the sulfur compounds depressed the denitrogenation of perhydroacridine at high temperature at which the hydrogenations of acridine to perhydroacridine attained equilibria. The addition of very small amounts of  $\text{CS}_2$ , as shown in Fig. 6, seems to slightly increase the concentration of dicyclohexylmethane with the reduced catalyst at  $360^\circ\text{C}$ . Since  $\text{CS}_2$  is easily decomposed to form  $\text{H}_2$ , the resulting  $\text{H}_2\text{S}$  may enhance the hydrodenitrogenation. However, the enhancement of the denitrogenation of perhydroacridine is not observed during the reaction. Hence, some  $\text{H}_2\text{S}$  present on the surface does not act as a sulfiding agent but may play an important role in the hydrodenitrogenation steps, for example, in the Hofmann degradation (19). Thus, the change in the product distribution on addition of  $\text{CS}_2$  differs from that of the other sulfide compounds added.

Figure 7 shows, however, that at  $300^\circ\text{C}$  with the reduced catalyst the concentrations of both dicyclohexylmethane and perhydroacridine decreased, and that of oc-

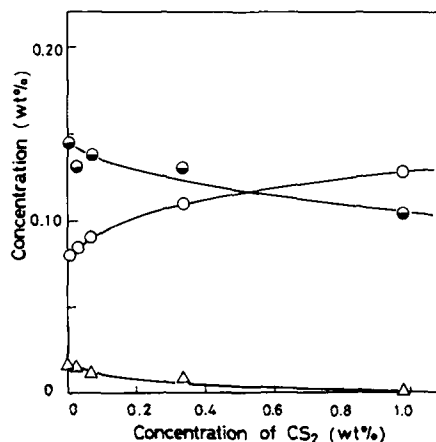


FIG. 7. Effect of  $\text{CS}_2$  on the products of acridine hydrodenitrogenation on the reduced catalyst at  $300^\circ\text{C}$ .  $\bullet$ , Perhydroacridine;  $\circ$ , octahydroacridine;  $\Delta$ , dicyclohexylmethane.

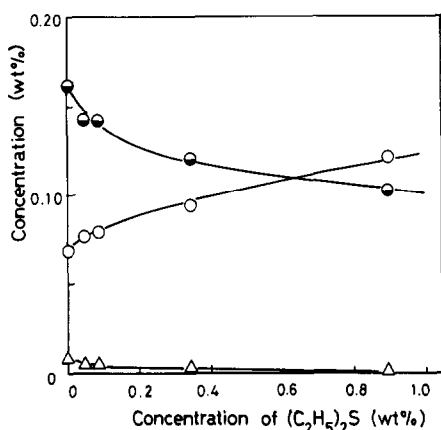


FIG. 8. Effect of  $\text{CS}_2$  on the products of acridine hydrodenitrogenation on the sulfided catalyst at  $300^\circ\text{C}$ .  $\circ$ , Octahydroacridine;  $\bullet$ , perhydroacridine;  $\Delta$ , dicyclohexylmethane.

tetrahydroacridine increased, on the addition of  $\text{CS}_2$ . This also agreed with the data obtained from the sulfided catalysts as shown in Fig. 8. Therefore, sulfur compounds appear to depress the hydrogenation of octahydroacridine to perhydroacridine at low temperature, as well as the hydrogenation of carbazole to tetrahydrocarbazole (unpublished data).

#### Effect of Oxygen Compounds on Acridine Hydrodenitrogenation

Figure 9 shows the effect of xanthene on the product composition of acridine hydrodenitrogenation on the reduced catalyst at  $360^\circ\text{C}$ . Since xanthene acts as a retarding agent in the same manner as the sulfur compounds, oxygen compounds also appear to depress the denitrogenation of perhydroacridine.

### DISCUSSION

#### Kinetics of the Retarding Effect

The studies of the hydrodenitrogenation of pyridine and quinoline found that nitrogen removal was pseudo-first order with respect to total nitrogen concentration but the apparent first-order rate constant decreased in magnitude as the nitrogen content of the feed increased (3). McIlvried (20) has stud-

ied the hydrodenitrogenation of pyridine and piperidine on a sulfided  $\text{NiMo}/\text{Al}_2\text{O}_3$  catalyst from 5.1 to 10.1 MPa at  $315^\circ\text{C}$  and reported that the rate expression was

$$r = kP_N P_H / (1 + K_N P_N + K_H P_H)$$

where N, H, and A represent piperidine, hydrogen, and ammonia, respectively. Sonnemans *et al.* (21) and Satterfield and Cocchetto (22) also proposed similar kinetic expressions for the hydrogenation of pyridine on a reduced  $\text{CoMo}/\text{Al}_2\text{O}_3$  catalyst and the hydrodenitrogenation of quinoline on a sulfided  $\text{NiMo}/\text{Al}_2\text{O}_3$  catalyst.

Nagai *et al.* (5) have also studied the kinetics of acridine hydrodenitrogenation on a reduced  $\text{Mo}/\text{Al}_2\text{O}_3$  catalyst and found the formation of dicyclohexylmethane to be one-half order in perhydroacridine concentration (0.05–0.4 wt%) and nine-tenths to two-tenths order in hydrogen partial pressure (2.2–13.0 MPa). The data for the rate of dicyclohexylmethane formation were represented by a Langmuir-type equation. Allowing for competitive adsorption of perhydroacridine (PA) and hydrogen (H), the following equation can be derived by a graphical method under a constant partial

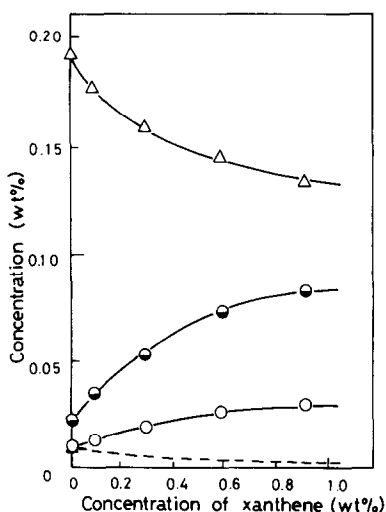


FIG. 9. Effect of xanthene on the products of acridine hydrodenitrogenation on the reduced catalyst at  $360^\circ\text{C}$ .  $\circ$ , Octahydroacridine;  $\bullet$ , perhydroacridine;  $\Delta$ , dicyclohexylmethane. ---, estimated concentration of benzylcyclohexane.

TABLE I  
 Parameter Values for Best Fits

Compound	$k$ (mmole/h g-cat)	$K_H$ (kPa <sup>-1</sup> )	$K_{PA}$ (kPa <sup>-1</sup> )	$K_A$ (kPa <sup>-1</sup> )	Variance
Dibenzothiophene	0.58	$18.0 \times 10^{-5}$	13.3	$16.7 \times 10^{-2}$	9.7
Benzothiophene	0.81	$8.6 \times 10^{-5}$	7.1	$6.8 \times 10^{-2}$	28
Thiophene	0.62	$10.0 \times 10^{-5}$	5.5	$5.1 \times 10^{-2}$	62
Dimethyl sulfide	0.96	$7.3 \times 10^{-5}$	9.0	$3.2 \times 10^{-2}$	9.7
Ethanthiol	0.82	$8.6 \times 10^{-5}$	8.2	$1.0 \times 10^{-2}$	10.9
Xanthene	0.90	$7.4 \times 10^{-5}$	8.8	$1.8 \times 10^{-3}$	0.9

pressure of either perhydroacridine or hydrogen (5):

$$r_{DCM} = kK_{PA}K_H P_{PA}P_H / (1 + K_{PA}P_{PA} + K_H P_H)^2 \quad (1)$$

where  $r$  is the formation of dicyclohexylmethane (DCM),  $k$  is a rate constant,  $K_i$  is an adsorption constant, and  $P_i$  is a partial pressure. This equation is based on a dual site mechanism where the denitrogenation (desulfurization or deoxygenation) and hydrogenation occur on different sites. All of the acridine compounds except perhydroacridine adsorbed on the hydrogenation sites, whereas perhydroacridine, hydrogen, and the sulfur and oxygen compounds adsorbed on the denitrogenation sites. The denitrogenation of octahydroacridine to benzylcyclohexane on the denitrogenation sites is neglected in Eq. (1) because the benzylcyclohexane concentration is much less than the dicyclohexylmethane concentration. Equation (1) is consistent with the results of quinoline hydrogenation by Shih (15).

In this work, Eq. (1) was applied to the retarding kinetics of the denitrogenation of perhydroacridine on a reduced Mo/Al<sub>2</sub>O<sub>3</sub> catalyst by the addition of sulfur and oxygen compounds at 360°C. There would be little possibility of ring hydrogenation prior to removal of sulfur or oxygen from the sulfur or oxygen aromatic compounds during the competitive reaction; the possibility was ignored because the nitrogen compounds adsorbed more strongly than these

compounds on the hydrogenation sites (9, 10). Since addition of the sulfur and oxygen compounds (A) inhibited the formation of dicyclohexylmethane, Eq. (1) becomes

$$r_{DCM} = kK_{PA}K_H P_{PA}P_H / (1 + K_{PA}P_{PA} + K_H P_H + K_A P_A)^2 \quad (2)$$

Equation (2) was linearized in the form

$$Y_A = (P_{PA}P_H/r)^{1/2} = 1/(kK_{PA}K_H)^{1/2} + P_{PA}K_{PA}/(kK_{PA}K_H)^{1/2} + P_H K_H / (kK_{PA}K_H)^{1/2} + P_A K_A / (kK_{PA}K_H)^{1/2} \quad (3)$$

A least-squares analysis was done in Eq. (3) to determine the parameters  $k$ ,  $K_{PA}$ ,  $K_H$ , and  $K_A$ , using the BASIC program technique for chemical engineering (23).

The most satisfactory fit to the data occurred with similar values of  $k$ ,  $K_H$ , and  $K_{PA}$  except for  $K_A$  and the lower variance, variance =  $(Y_{A,obs} - Y_{A,cal})^2$ . Parameter values for the best correlations are given in Table 1. A large adsorption constant of a high molecular weight sulfur compound produced a strong inhibitor. But xanthene, which is an oxygen compound, was the weakest inhibitor. The adsorption constant of xanthene was 93 times smaller than that of dibenzothiophene, a structure similar to xanthene. The results suggest that an oxygen compound weakly depresses the denitrogenation. The adsorption constants of hydrogen and perhydroacridine were about  $8.4 \times 10^{-5}$  and 7.5, respectively. Broderick and Gates (24) have studied the dibenzo-

thiophene hydrodesulfurization on a sulfided CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst and reported that the adsorption constant of hydrogen is  $8 \times 10^{-5} \text{ kPa}^{-1}$  at 325°C on the basis of the equation  $r = kC_{\text{DBT}}C_{\text{H}}/(1 + K_{\text{DBT}}C_{\text{DBT}} + K_{\text{H}_2\text{S}}C_{\text{H}_2\text{S}} + K_{\text{H}}C_{\text{H}})^2$ . Also, Kilanowski and Gates (25) reported that both adsorption constants of benzothiophene and hydrogen sulfide are  $6 \times 10^{-2} \text{ kPa}^{-1}$  at 332.5°C on the basis of the equation  $r = kP_{\text{BT}}P_{\text{H}}/(1 + K_{\text{BT}}P_{\text{BT}} + K_{\text{H}_2\text{S}}P_{\text{H}_2\text{S}})^2$ . Thus, the adsorption constants of hydrogen and benzothiophene in Table 1 are similar in order of magnitude to those found at 332.5°C. These constants are considered reasonable.

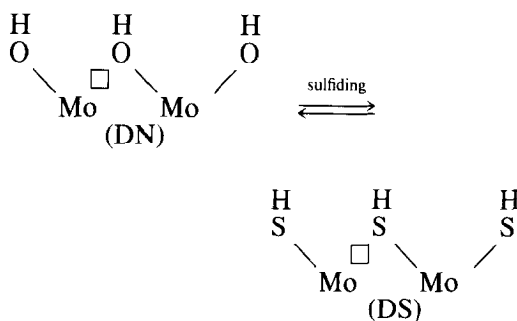
The kinetic study supports the idea that the sulfur and oxygen compounds adsorb competitively with perhydroacridine on denitrogenation sites and result in inhibiting the denitrogenation of perhydroacridine. Furthermore, we have studied the effect of the sulfur and oxygen compounds on dibenzothiophene hydrodesulfurization and found that the sulfur and oxygen compounds depressed the dibenzothiophene desulfurization but not the hydrogenation on the sulfided Mo/Al<sub>2</sub>O<sub>3</sub> catalyst (9), suggesting the same dual reaction mechanism. Consequently, the same conclusion was obtained from both hydrodenitrogenation and hydrodesulfurization. Denitrogenation, desulfurization, and deoxygenation appear to occur competitively on one type of site on the sulfided and reduced Mo/Al<sub>2</sub>O<sub>3</sub> catalyst, whereas hydrogenation occurs exclusively on the other site.

#### Active Sites

The activity for dicyclohexylmethane formation was decreased to 50% when the reduced catalyst was sulfided, while the apparent activation energy for the sulfided catalyst rose 21 to 156 kJ/mole from that of the reduced catalyst. This result suggests that sulfiding decreases the strength of denitrogenation sites. Furthermore, more of hydrogenated nitrogen compounds were produced with the sulfided catalyst than with the reduced catalyst. Massoth (26) has

studied the rates and stoichiometry of sulfiding Mo/Al<sub>2</sub>O<sub>3</sub> catalysts and reported that a sulfided Mo/Al<sub>2</sub>O<sub>3</sub> catalyst held more hydrogen on a sulfided anion associated with a molybdenum atom than a reduced Mo/Al<sub>2</sub>O<sub>3</sub> catalyst. An SH group on molybdenum produced by sulfiding is likely to be more effective for hydrogenation than an OH group. This is in agreement with hydrogenation that is associated with Brønsted acid sites of molybdenum on the sulfided NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst (11).

Furthermore, Massoth (26) proposed that the activity for thiophene hydrodesulfurization depended on a terminal sulfur anion vacancy (□) and further suggested that NH<sub>3</sub> was not held more strongly on an □S pair as compared to an □O pair:



(DN and DS represent denitrogenation and desulfurization, respectively.) His proposal of active sites for desulfurization leads us to assume a particular kind of site for the denitrogenation of perhydroacridine in the hydrodenitrogenation of acridine on the Mo/Al<sub>2</sub>O<sub>3</sub> catalyst. Perhydroacridine is considered to adsorb more strongly on an □O pair than an □S pair analogous with the adsorption of NH<sub>3</sub>, and is denitrogenated. Sulfidation decreases the number of □O pairs while increasing the number of □S pairs and, consequently, the denitrogenation of perhydroacridine is depressed. Thus, the denitrogenation may take place on an □O pair rather than on an □S pair on a molybdenum atom. Therefore, denitrogenation seems to be sensitive to the structure. Desulfurization appears to depend on an □O pair as well as an □S pair and is an



insensitive reaction. The cooperative mechanism of terminal oxygen (sulfur) anion and anion vacancy for hydrodenitrogenation will be discussed in a later paper.

#### CONCLUSIONS

The following conclusions emerge from this study:

(1) Sulfiding of the reduced catalyst hindered the denitrogenation of perhydroacridine to dicyclohexylmethane at all reaction temperature.

(2) Sulfur and oxygen compounds depressed the denitrogenation at higher temperatures at which the intermediate hydrogenations of acridine to perhydroacridine attained equilibria.

(3) At lower temperatures the sulfur compounds depressed the hydrogenation of octahydroacridine to perhydroacridine resulting in reduction of the denitrogenation of perhydroacridine.

(4) Kinetics of the retarding effect was determined with a reduced Mo/Al<sub>2</sub>O<sub>3</sub> catalyst at 360°C, on the assumption of the competitive desorption of perhydroacridine, a sulfur and oxygen compound, and hydrogen on one kind of catalytic site and of octahydroacridine on the other.

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