

Hydrogenation of Aromatic Hydrocarbons  
Catalyzed by Sulfided  $\text{CoO-MoO}_3/\gamma\text{-Al}_2\text{O}_3$ :  
Reactivities, Reaction Networks, and Kinetics

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INTRODUCTION

Accompanying the recent emphasis on new energy sources, there has been a surge of development work on processes for upgrading heavy fossil fuels, including coal liquids, shale oil, tar sands, and petroleum residua. Upgrading is normally effected by hydrotreating in the presence of catalysts like "cobalt molybdate" or "nickel molybdate" at 50-250 atm and 300-450°C (1). In these applications, the principal catalytic reactions are hydrodesulfurization, hydrodenitrogenation, hydrodeoxygenation, hydrocracking, and hydrogenation of aromatics. Among the slowest of these reactions are the aromatic hydrogenations, which take on great importance because hydrodenitrogenation of polycyclic aromatics does not take place until ring saturation has occurred (2). It therefore appears that with the best available catalysts, hydrogenation of aromatics is the class of hydroprocessing reactions most deserving of careful study.

Hydrogenation of aromatics is also important in developing coal liquefaction technology exemplified by the donor solvent process and some forms of the solvent refined coal process (3); in these processes the product liquid undergoes catalytic hydrogenation and is then recycled to the liquefaction reactor, where it transfers hydrogen to the liquefying coal (4).

The literature of catalytic hydroprocessing provides only fragmentary information about the reaction networks, reactivities, and kinetics in aromatic hydrogenation, most of the work having been done with unpromoted catalysts at conditions far removed from those of industrial interest (5). The reported kinetics data for hydrogenation of aromatics in the presence of promoted sulfided catalyst like "cobalt molybdate" are limited to benzene, cyclohexene, toluene, phenanthrene, and naphthalene (6-11).

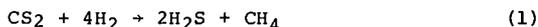
The experiments reported here were carried out to establish the reactivities and reaction networks for hydrogenation of benzene, biphenyl, naphthalene, and 2-phenylnaphthalene as well as detailed kinetics of biphenyl hydrogenation in the presence of a commercial catalyst (sulfided "cobalt molybdate,"  $\text{CoO-MoO}_3/\gamma\text{-Al}_2\text{O}_3$ ). The relative reactivities and reaction networks were determined at a pressure (75 atm), and temperature (325°C) representative of industrial conditions. The biphenyl kinetics experiments were done over a pressure range of 64-200 atm and a temperature range of 300-375°C.

Biphenyl and 2-phenylnaphthalene were chosen as model reactants in part because they are the principal aromatic products formed in the hydrodesulfurization of dibenzothiophene and of benzo[b]naphtho[2,3-d]-

thiophene, respectively (12,13). The latter two compounds are typical of the least reactive sulfur-containing compounds found in the heavier petroleum residua and coal-derived liquids. Naphthalene was chosen because upon hydrogenation it forms tetralin, the most widely used model compound used as a hydrogen donor in coal liquefaction experiments.

#### EXPERIMENTAL

The experiments designed to determine relative reactivities were carried out in a commercial one-liter batch reactor (Autoclave Engineers). The design of the autoclave allowed charging of the catalyst after the reactants had been brought to reaction temperature, thereby virtually eliminating any heat-up period which would prevent elucidation of isothermal kinetics from the conversion data (14). The catalyst was particles ( $\sim 150\mu\text{m}$ ) of  $\text{CoO-MoO}_3/\gamma\text{-Al}_2\text{O}_3$  (American Cyanamid HDS 16A), 2g of which were externally sulfided at  $400^\circ\text{C}$  with 10 vol%  $\text{H}_2\text{S}$  in  $\text{H}_2$  at atmospheric pressure for two hours prior to being charged to the reactor. The reactant solution (375 ml) contained roughly 0.75 mole% of the hydrocarbon reactant in *n*-hexadecane (Humphrey Chemical Co., redistilled). The solution was saturated with hydrogen at the reaction temperature, providing a large stoichiometric excess of this reactant. The reactor was operated at  $75 \pm 2$  atm and  $325 \pm 1^\circ\text{C}$  in all the experiments. Carbon disulfide, 0.1 mole%, was added to the reaction mixture. It was found that this source of sulfur in the reactant was essential to maintain the activity of the catalyst by maintaining it in the sulfided form (15). The  $\text{CS}_2$  was almost instantaneously converted into  $\text{H}_2\text{S}$  under the reaction conditions, the rate of the hydrogenolysis reaction



being at least 8000 times greater than that of the aromatic hydrogenation reactions.

The biphenyl kinetics studies were carried out using a high-pressure flow microreactor, the design and operation of which are described elsewhere (16). The reactor operated with solid particles of catalyst and a liquid reactant phase saturated with hydrogen.

The operating conditions of the flow reactor used for the kinetics experiments are summarized in Table 1.

TABLE 1. Operating conditions for the flow reactor

Catalyst: commercial  $\text{CoO-MoO}_3/\gamma\text{-Al}_2\text{O}_3$  (American Cyanamid HDS 16A)  
mass: 0.025-0.050g diluted with particles of alundum  
particle size:  $150\mu\text{m}$   
volume of catalyst bed:  $0.325\text{ cm}^3$   
length of bed: 4.0 cm  
Catalyst pretreatment: sulfided in situ with 10%  $\text{H}_2\text{S}$  in  $\text{H}_2$  for two hours at  $400^\circ\text{C}$   
Reactor pressure: 64-200 atm  
Temperature:  $300\text{-}375^\circ\text{C}$   
Biphenyl concentration:  $5\text{-}25 \times 10^{-3}$  gmoles/liter  
Cyclohexylbenzene concentration:  $0\text{-}13 \times 10^{-3}$  gmoles/liter  
Carbon disulfide concentration:  $4\text{-}18 \times 10^{-3}$  gmoles/liter  
Hydrogen concentration:  $100\text{-}450 \times 10^{-3}$  gmoles/liter  
Liquid flow rate:  $0.2\text{-}60\text{ cm}^3/\text{hr}$ .  
Solvent (carrier oil): *n*-hexadecane.

### Materials:

The reagents naphthalene (>99%) and benzene (>99%) were supplied by Fisher; bicyclohexyl (>98%), cyclohexylbenzene (>98%), and tetralin (>99%) by Aldrich; biphenyl (>98%) by Eastman; and 2-phenylnaphthalene (>98%) by ICN Pharmaceuticals. All these reagents were used without further purification.

### Product analysis:

The product samples from the flow reactor were analyzed with an Antek 440L gas chromatograph equipped with a flame ionization detector. The column was packed with methylsilicone on 100-200 mesh Supelcoport (GP 3% SP-2100 DB) operated at 140°C.

The product samples drawn periodically from the batch reactor were analyzed with a Perkin-Elmer 3920 B gas chromatograph equipped with a flame ionization detector and a 0.8 mm-O.D. X 0.025 mm-I.D. X 100-m-long wall-coated open tubular column (the liquid phase was OV-101, Perkin Elmer) with an all-glass splitter injector. The column temperature was varied depending on the reactant compound, and temperature programming was used to improve peak resolution.

Principal reaction products formed from benzene, biphenyl, and naphthalene were identified by comparing glc retention times of the known compounds with retention times of components of the product mixtures. For identification of the primary products of 2-phenylnaphthalene hydrogenation, tricarbonylchromium complexes of the products were synthesized using chromium hexacarbonyl (17). The tricarbonyl chromium complexes which were formed were separated by the column chromatography technique on an alumina (4% water) column. The hydrocarbon solvent and uncomplexed material were eluted with n-pentane. The separation of the complexes on the column was achieved by using different proportions of n-pentane and methylene chloride. The structures of the recrystallized complexes were determined by proton NMR spectroscopy; details of this technique are given elsewhere (13).

From these product analyses, conversion-time data were obtained for each set of reactants and products in the batch reactor experiments. In the flow reactor, differential conversions were measured to determine rate data directly. The rate data were obtained over a wide range of independent variables; mixed feeds were used, including the reaction products in widely varied concentrations.

### RESULTS AND DISCUSSION

Figure 1 shows the principal products and the reaction networks for the aromatic compounds studied in the batch reactor. In all these experiments, mass balances obtained from the unconverted reactant and the products were good. Naphthalene analysis was extremely good, and mass balance of more than 98% was observed for all the samples.

In the flow-reactor experiments a linear relation between conversion and inverse space velocity was observed up to about 15% biphenyl conversion, demonstrating that all the data reported here represented differential conversions. These low-conversion data always showed more than 99% mass balance.

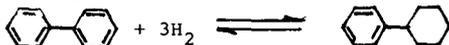
Blank experiments performed in the batch reactor with hydrogen and biphenyl and with hydrogen and cyclohexylbenzene confirmed that there was no observable conversion of these reactants even under more severe conditions (400°C and 100 atm), indicating that all the observed reactions were catalytic. These results are consistent with the thermochemical calculations reported by Ross et al. (20), showing the extreme stability of the C-C bond towards homolysis and free radical formation in the molecules like biphenyl and naphthalene.

In batch experiments with benzene, cyclohexane was observed as the only primary product. The concentration-time profiles for the benzene reaction are shown in Fig. 2. The unidentified hydrocarbon indicated in the benzene reaction network (Fig. 1) was not separated in the glc analysis. The benzene-cyclohexane reaction is reversible and is well documented in the literature (5), and so experiments with cyclohexane as a reactant were not done.

The most thorough set of experiments was carried out with biphenyl, which reacted with hydrogen to give cyclohexylbenzene as a primary product. Cyclohexylbenzene was subsequently converted into bicyclohexyl. The concentration-time plots for the biphenyl reaction network are shown in Fig. 3; the data clearly show that bicyclohexyl is a secondary product, since the slope of the curve at zero time is zero.

Three unidentified hydrocarbon products having very nearly equal retention times on the glc column were also observed in small quantity (in total, about 10% at the maximum conversion). Hydrogenation experiments carried out with cyclohexylbenzene and with bicyclohexyl as the reactants showed that these hydrocarbons were formed as primary products from cyclohexylbenzene, but not from bicyclohexyl. The comparison of the glc retention times of these products with those of several possible products obtained from ring opening (substituted benzene or cyclohexane) and substituted indane and tetralin suggest that these products were not obtained by cracking of biphenyl or by C-C bond cleavage followed by ring closure. Urimoto et al. (18) performed dibenzothiophene hydrodesulfurization experiments and observed 3-methylcyclopentylcyclohexane and 3-3'-dimethyldicyclopentyl products using a catalyst and reaction conditions similar to those used in this work, which indicates the occurrence of isomerization reactions. During hydroprocessing reactions, isomerization of cyclohexane to methylcyclopentane and of tetralin to methyl indane is reported in the literature (5,19). This information suggests that the three unidentified products could be isomerized products formed from cyclohexylbenzene--for example, methylcyclopentylbenzene.

These three products together are represented as hydrocarbons in the reaction network shown in Fig. 1. In experiments with hydrogen and cyclohexylbenzene as reactants, biphenyl was formed, indicating that the primary hydrogenation reaction,



is reversible. The experiments in the flow reactor were designed to determine the nonlinear rate expression for this primary hydrogenation-dehydrogenation reaction. Fig. 4 shows a typical set of data obtained at 350°C. The differential conversion experiments were done at 300, 325, 350 and 375°C; the full set of rate data was fitted with a non-

linear least squares technique (21). The following rate expression represents the data with a high degree of accuracy, but several other equations (similar in form) provide comparable fits. Work on discrimination of the equations is continuing; this rate expression should be considered tentative:

$$r = \frac{k K_{\text{BPH}} K_{\text{H}_2}^3 (C_{\text{BPH}} C_{\text{H}_2}^3 - \frac{1}{K_E} C_{\text{CHB}})}{(1.0 + K_{\text{BPH}} C_{\text{BPH}} + K_{\text{H}_2} S C_{\text{H}_2} S)^2 (1.0 + K_{\text{H}_2} C_{\text{H}_2})^2} \quad (2)$$

$$k = 8 \times 10^7 \exp\left(-\frac{32,000}{RT}\right)$$

$$K_{\text{BPH}} = 4.5 \times 10^{-5} \exp\left(\frac{14,000}{RT}\right)$$

$$K_{\text{H}_2} S = 1.6 \times 10^{-4} \exp\left(\frac{13,000}{RT}\right)$$

$$K_{\text{H}_2} = 4.25 \exp\left(\frac{4,000}{RT}\right)$$

$$K_E = 2.2 \times 10^{-3} \exp\left(\frac{16,500}{RT}\right)$$

BPH = biphenyl, H<sub>2</sub> = hydrogen, CHB = cyclohexylbenzene

The smooth lines in Fig. 4 are the predictions based on the above equation. It is clear that this equation fits the data well.

In batch experiments, naphthalene was hydrogenated to give 1,2,3,4-tetrahydronaphthalene (tetralin) as a primary product. Tetralin was further hydrogenated to give cis- and trans-decahydronaphthalene (decalin). Time-concentration profiles for naphthalene and its reaction products are presented in Fig. 5. From these data, it is evident that equilibrium is approached between tetralin and naphthalene.

In experiments with hydrogen and tetralin as reactants, naphthalene was formed, indicating that the primary hydrogenation reaction is reversible. Trans-decalin was the predominant isomer of decalin. No other hydrocarbon products were detected.

Hydrogenation of 2-phenylnaphthalene gave two primary products, 2-phenyltetralin and 6-phenyltetralin, each of which experienced further hydrogenation. The concentration-time profiles are presented in Fig. 6. The secondary products are represented together as hydrocarbons in this analysis, consisting chiefly of phenyl-substituted decalins. 2-Phenyltetralin or 6-phenyltetralin are not commercially available, and experiments were not performed with these as reactants to demonstrate whether the primary hydrogenation reactions were reversible. But on the basis of the experience with biphenyl and naphthalene, it was assumed that the primary hydrogenation reactions are reversible. It can be seen from the data presented in Fig. 6 that equilibrium is approached between 2-phenylnaphthalene and its two primary products, 2-phenyltetralin and 6-phenyltetralin.

In contrast to these hydrogenation reactions, hydrodesulfurization reactions are practically irreversible, and the conversion data for the individual sulfur-containing compounds follow pseudo-first order behavior (23). As the primary hydrogenation reactions studied here are reversible, a deviation from the pseudo-first order behavior was observed as equilibrium was approached. The pseudo-first order rate constants for the overall disappearance of the component, determined from the low conversion data, are summarized in Table 2. For the determination of rate constants to represent the reaction networks from the high conversion data, it was assumed that each reaction in the network was pseudo-first order in the organic reactant. All the reversibilities were taken into account in representing quantitative kinetics for the complete reaction networks. The pseudo-first order rate constants were estimated from the full set of data determined in the experiments with each organic reactant, as follows: (1) In the case of benzene and biphenyl, raw concentration versus time data were smoothed by fitting spline functions using the IMSL subroutine ICSMOU (24); this program performs one dimensional data smoothing by error detection and is highly effective in smoothing a data set only mildly contaminated with isolated errors; (2) the smoothed data were used with equal weighting in the Carlton 2 program (25) to determine best values of the individual rate constants. The values of the rate constants for the individual reactions in the networks are shown in Fig. 1. The lines in Figs. 2,3,5,6 represent the model predictions from the estimated pseudo first-order rate constants based on the individual reaction networks shown in Fig. 1.

TABLE 2. Pseudo-first order rate constants for hydrogenation catalyzed by sulfided CoO-MoO<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub> at 325°C and 75 atm.

Reactant	Concentration, mole%	10 <sup>6</sup> X Pseudo-first order rate constant m <sup>3</sup> /kg of catalyst·sec <sup>a</sup>
Benzene	0.65	2.8 ± 0.1
Biphenyl	0.80	3.0 ± 0.2
Naphthalene	0.85	58.9 ± 3.6
2-Phenyl-naphthalene	0.75	61.4 ± 5.3

<sup>a</sup>Data are reported with 95% confidence limits.

The final conversion levels for naphthalene and 2-phenyl-naphthalene were of the order of 99%, whereas biphenyl and benzene were only about 75% converted after completion of the experiments. Experiments were carried out for long periods so that good estimates of the equilibrium constants could be obtained from the conversion data. The equilibrium constant for the biphenyl hydrogenation,  $K_E = [CCHB/CBPH \cdot CH_2^3]_{\text{equil.}} = 365$ , obtained from the above analysis of the kinetics, agrees fairly well with Frye's (26) gas-phase equilibrium experiments. At 325°C his data indicate  $K_E$  to be equal to 485.

From these networks, it can be seen that primary products obtained by aromatic hydrogenation are hydroaromatics, potential hydrogen donors which can readily be dehydrogenated in the presence of liquefying coal. The relative hydrogen-donor capacity of several

hydroaromatics was determined by Doyle (22), his results showing that tetralin or substituted tetralins are much better hydrogen donors than cyclohexylbenzene.

Liquefaction of coal has been shown to occur almost instantaneously upon reaching a high temperature in the presence of a hydrogen-donor solvent (27). Thus the slow steps in the hydrogenation/liquefaction process may be the hydrogenation of the recycle solvent to replenish hydrogen donor species (28). One of the objectives in the solvent hydrogenation is to maximize the yield of hydroaromatics. The reactions leading to consumption of hydroaromatic (for example, further hydrogenation of tetralin to decalins or isomerization of hydroaromatics) are undesirable, as they result in a solvent of reduced hydrogen-donor capacity. From Fig. 1 it is evident that these undesirable side reactions are relatively slow compared with the primary hydrogenation reactions. Under the experimental conditions of this study, the hydrogenation-dehydrogenation equilibrium was favorable towards higher yields of hydroaromatics. The biphenyl kinetics indicates that at higher temperatures dehydrogenation reactions are more significant, which suggests a strategy of maximizing yields of hydroaromatics by applying lower temperatures and high hydrogen partial pressures. The catalyst would also play an important role; the ideal catalyst would have moderate hydrogenation activity to hydrogenate the solvent to constituents like tetralin. But it should not have excessive activity to over-hydrogenate and form poor hydrogen donors like decalin, the formation of which would also represent excessive consumption of the costly hydrogen.

Ahuja et al. (7) ascribed the isomerization of cyclohexane to methylcyclopentane to the acidity of the support, and it follows from their suggestion that the isomerization of hydroaromatics would be less if less acidic catalyst supports (like  $\text{SiO}_2$ ) were used. The isomerization reactions are significantly inhibited by nitrogen-containing compounds (7), hence the feeds with higher concentrations of nitrogen-containing compounds might seem to be favorable--except that nitrogen-containing compounds also strongly inhibit the hydrogenation reactions (2).

The results of Table 1 show that benzene and biphenyl have nearly the same reactivity; naphthalene and 2-phenylnaphthalene have nearly equal reactivities, one order of magnitude less than that of benzene. The high-pressure, high-temperature hydrogenation of benzene and naphthalene reported to occur in the presence of unsupported  $\text{MoS}_2$  and  $\text{WS}_2$  catalysts, indicates a 17-fold higher reactivity of naphthalene in comparison with benzene (5), which agrees well with the results reported in Table 1.

Naphthalene has a resonance energy of 75 kcal/mole, which is less than twice that of benzene's 42 kcal/mole (29), i.e., the rings in naphthalene are less aromatic in character than that of benzene and so more easily reduced, which explains the higher reactivity of naphthalene.

#### REFERENCES

- (1) Gates, B. C., Katzer, J. R., and Schuit, G. C. A., "Chemistry of Catalytic Processes," Chap. 5, McGraw-Hill, New York (1979).
- (2) Bhide, M. V., Ph.D. thesis, University of Delaware (1979).
- (3) National Academy of Sciences, Assessment of Technology for Liquefaction of Coal, Washington, D.C., 1977.
- (4) Furlong, L. E., Effron, E., Vernon, L. W., and Wilson, E. L., Chem. Eng. Progr., 72 (8), 69 (1976).
- (5) Weisser, O., and Landa, S., "Sulphide Catalysts, Their Properties and Applications," Pergamon, New York, 1973.
- (6) Voorhoeve, R. J. H., and Stuiver, J. C. M., J. Catal., 23, 228 (1971).
- (7) Ahuja, S. P., Derrien, M. L., and LePage, J. F., Ind. Eng. Chem. Prod. Res. Develop., 9, 272 (1970).
- (8) Huang, C. S., M.S. thesis, University of Mississippi (1976).
- (9) Rollmann, L. D., J. Catal., 46, 243 (1977).
- (10) de Beer, V. H. J., Dahlmans, J. G. S., and Smeets, J. G. M., J. Catal., 42, 467 (1976).
- (11) Hagenbach, G., Courty, Ph., and Delmon, B., J. Catal., 23, 295 (1971).
- (12) Houalla, M., Nag, N. K., Sapre, A. V., Broderick, D. H., and Gates, B. C., AIChE J., 24, 1015 (1978).
- (13) Sapre, A. V., Broderick, D. H., Fraenkel, D., Gates, B. C., and Nag, N. K., AIChE J., in press.
- (14) Shih, S. S., Katzer, J. R., Kwart, H., and Stiles, A. B., Preprints, ACS Div. Petrol. Chem., 22, 919 (1977).
- (15) Sapre, A. V., Ph.D. Thesis, University of Delaware, in preparation.
- (16) Eliezer, K. F., Bhide, M., Houalla, M., Broderick, D. H., Gates, B. C., Katzer, J. R., and Olson, J. H., Ind. Eng. Chem. Fundam., 16, 380 (1977).
- (17) Nicholls, B., and Whiting, M., J. Chem. Soc. (London), 551 (1959).
- (18) Urimoto, H., and Sakikawa, N., Sekiyu Gakkaiishi, 15, 926 (1972).
- (19) Cronauer, D. C., Jewell, D. M., Shah, Y. T., and Kueser, K. A., Ind. Eng. Chem. Fundam., 17 (4), 291 (1978).

- (20) Ross, D. S. and Blessing, J. E., Prepr. ACS Div. Fuel Chem. 24, 129 (1979).
- (21) NLLS program, University of Delaware Computing Center.
- (22) Doyle, G., Prepr. ACS Div. Petrol. Chem., 21, 165 (1975).
- (23) Nag, N. K., Sapre, A. V., Broderick, D. H., and Gates, B. C., J. Catal., 57, 509 (1979).
- (24) ICSSMOU, computer subroutine, International Mathematical and Statistical Library.
- (25) Himmelblau, D. M., Jones, C. R., and Bischoff, K. B., Ind. Eng. Chem. Fundam., 6, 539 (1967).
- (26) Frye, C. G., J. Chem. Eng. Data, 7, 592 (1962).
- (27) Whitehurst, D. D., and Mitchell, T. D., Prepr. ACS Div. of Fuel Chem., 21 (5), 127 (1976).
- (28) Guin, J. A., Tarrer, A. R., Lee, J. M., Lo, L., and Curtis, C. W., Ind. Eng. Chem. Proc. Des. Dev., 18, 371 (1979).
- (29) Pauling, L., "The Nature of The Chemical Bond," Cornell University Press, 1967.

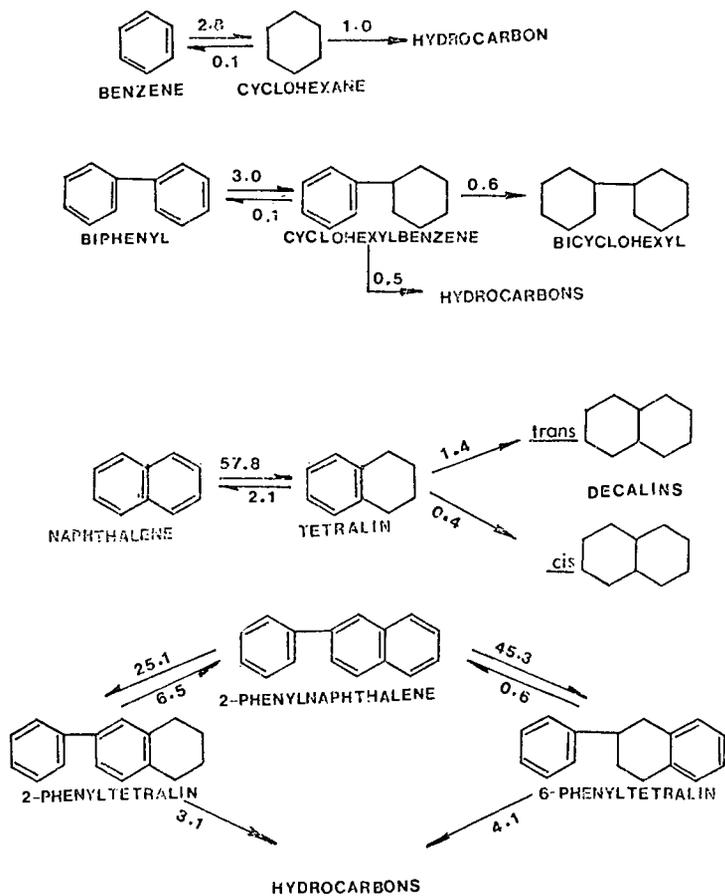


Fig. 1: Reaction networks for hydrogenation of benzene, biphenyl, naphthalene, and 2-phenylnaphthalene in the presence of sulfided  $\text{CO-MoO}_3/\gamma\text{-Al}_2\text{O}_3$  at  $325^\circ\text{C}$  and 75 atm. Each reaction is approximated as first order in the organic reactant; the numbers next to the arrows are the pseudo first order rate constants in  $10^9 \times$  cubic meters per kilogram of catalyst per second.

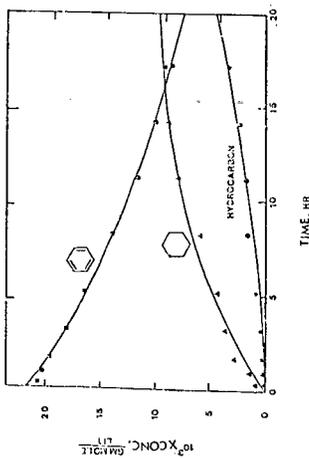


Fig. 2: Conversion of benzene and  $H_2$  in the presence of sulfided  $CoO-MoO_3/\gamma-Al_2O_3$  in a batch reactor at  $325^\circ C$  and 75 atm. The curves are the predictions of the reaction network model of Fig. 1.

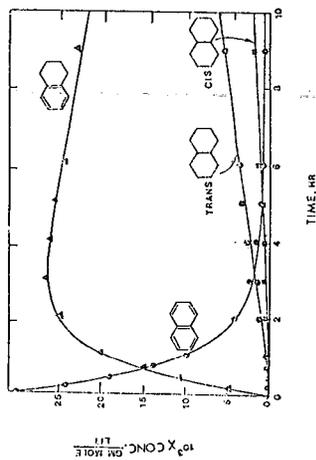


Fig. 5: Conversion of naphthalene and  $H_2$  in the presence of sulfided  $CoO-MoO_3/\gamma-Al_2O_3$  in a batch reactor at  $325^\circ C$  and 75 atm. The curves are the predictions of the reaction network model of Fig. 1.

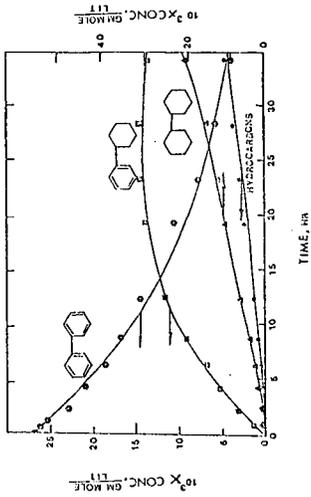


Fig. 3: Conversion of biphenyl and  $H_2$  in the presence of sulfided  $CoO-MoO_3/\gamma-Al_2O_3$  in a batch reactor at  $325^\circ C$  and 75 atm. The curves are the predictions of the reaction network model of Fig. 1.

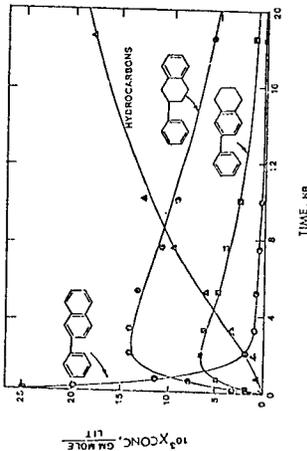


Fig. 6: Conversion of 2-phenylnaphthalene and  $H_2$  in the presence of sulfided  $CoO-MoO_3/\gamma-Al_2O_3$  in a batch reactor at  $325^\circ C$  and 75 atm. The curves are the predictions of the reaction network model of Fig. 1.

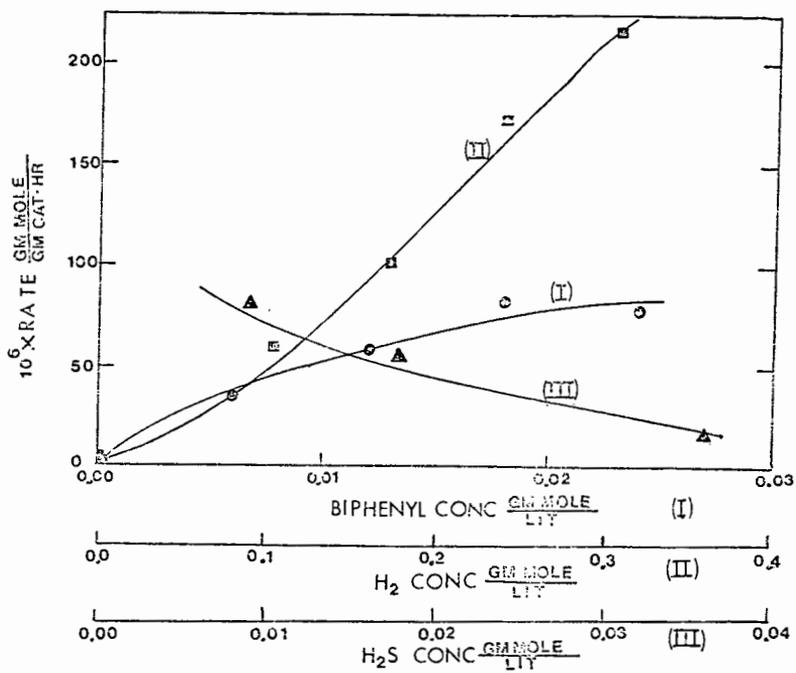


Fig. 4: Rate of biphenyl hydrogenation as a function of hydrogen,  $\text{H}_2\text{S}$ , and biphenyl concentrations at  $350^\circ\text{C}$ . The curves are cubic spline fits through individual points predicted by rate equation given in the text, for the actual concentrations at each point.