STERIC EFFECTS IN PHENANTHRENE AND PYRENE HYDROGENATION CATALYZED BY SULFIDED Ni-W/Al_2O_3

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The increased interest in coal liquefaction and catalytic upgrading of coal-derived liquids has recently led to a considerable amount of work on hydrodesulfurization and hydrodenitrogenation of model heterocyclic compounds in the presence of sulfided catalyst systems(1,2). In contrast, hydrogenation reactions of model polycyclic aromatic hydrocarbons in the presence of such catalysts have been studied to a limited extent (3-5). It is also noteworthy that in comparison with previous extensive studies on mechanistic and stereochemical aspects of metal-catalyzed hydrogenation of condensed aromatics, so far little attention has been paid to such aspects in hydrogenation studies with the structurally different class of sulfided catalysts.

In the present work the hydrogenation of phenanthrene (1) and pyrene (9) was systematically investigated as a function of sulfided catalyst type, reaction temperature, hydrogen pressure, and catalyst/feed ratio. Experiments were performed in a semi-batch reactor, and products obtained were identified and quantitatively analyzed by a combination of gas chromatography, PMR, and mass-spectral methods (see Experimental).

RESULTS AND DISCUSSION

Relative catalytic activities of sulfided Ni-Mo/Al_2O_3 (catalyst A), Ni-W/Al_2O_3 (catalyst B) and Co-Mo/Al_2O_3 (catalyst C) for hydrogenation of 1 were examined by comparative experiments under mild experimental conditions, i.e. pressure, 1500 psig; temperature, 341°C; reaction time, 2 hr. Under such conditions conversion of 1 into perhydrophenanthrene (8) is incomplete and the product contains, in addition to 8, a series of partially hydrogenated compounds expected from stepwise hydrogenation of phenanthrene (P), i.e. 9,10-dihydroP(2), 1,2,3,4-tetrahydroP(3), 1,2,3,4,9,10,11,12-octahydroP(4), 1,2,3,4,5,6,7,8-octahydroP(5), and isomeric mixtures of decahydroP(6) and dodecahydroP(7). With samples of the above indicated types of catalysts, having comparable concentrations of the active components and nearly identical surface areas and pore volumes, it was found that the decrease in H-aromaticity is 20-25% higher with A and B, as compared with C. Further, under conditions leading to complete saturation of 1 (2,900 psig; 341°C; 7 hr) the hydrogenation selectivity of B was found to be somewhat higher than that of A. Consequently, a catalyst of type B (containing 5.1% of NiO and 20.2% of WO_3; see Experimental) was selected for the hydrogenation study.

Figures 1 and 2 summarize the observed change in product composition from hydrogenation of 1 as a function of temperature in the range of 200-380°C. For the purpose of clarity the composition is plotted in two sets corresponding to anticipated consecutive stages of the hydrogenation process, i.e. an early stage (A) showing the change in concentration of phenanthrene derivatives with one or two hydrogenated rings (Fig. 1), and a later stage showing the change in concentration of derivatives with two or three hydrogenated rings (Fig. 2). Extrapolation of the curves in Fig. 1 to temperatures below 200°C, clearly indicates that 1,2,3,4-tetrahydroP(3) is the main primary product, while the other possible primary product, i.e., 9,10-dihydroP(2), is formed in considerably lower yield. The gradual decrease in the concentration of compound 3 with increase in temperature (Fig. 1) is accompanied by a corresponding increase in the yield of 1,2,3,4,5,6,7,8-octahydroP(5), a product which should be formed by hydrogenation of the residual aromatic end ring in 3. On the other hand, the gradual disappearance of 9,10-dihydroP(2) with temperature is not accompanied by

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any significant formation of the expected second-step hydrogenation product from 2, i.e., 1,2,3,4,9,10,11,12-octahydroP(4). Since conversion of 2 into 3 is a slow, indirect reaction (vide infra), these results indicate that 2 is not an important intermediate in the overall hydrogenation process leading to perhydrophenanthrene (8). After reaching a maximum of ∿60% b.wt. near 300°C, the concentration of 1,2,3,4,5,6,7,8-octahydroP(5) decreases with further increase in temperature. Figure 2 indicates that hydrogenation of the residual inner aromatic ring in 5, leading to the final product 8, involves the formation of olefinic intermediates, i.e. isomeric mixtures of decahydroP(6) and of dodecahydroP(7). Patterns similar to those indicated in Figs. 1 and 2 are also observed in the study of product composition as a function of hydrogen pressure (between 500-2,900 psig), and of catalyst/phenanthrene ratio.

The results obtained can be rationalized by considering, among other factors, the stereochemistry of the intermediate compounds formed in the stepwise hydrogenation of 1 to 8:

Initiation of the process by hydrogenation of the inner ring in 1 at the 9,10-position produces a somewhat strained hydroaromatic ring. In forming this ring the two aromatic end rings are forced out of coplanarity, and the resulting 9,10-dihydroP(2) shows strong dehydrogenation tendency at temperatures ≥250°C (vide infra). In contrast, hydrogenation of an end ring in 1, to yield 3, involves formation of a strainless hydroaromatic ring. Fast consecutive hydrogenation of the two end rings in 1 should produce 1,2,3,4,5,6,7,8-octahydroP(5), which is indeed observed as the main intermediate in the process. Examination of steric models of 5 indicates that flatwise adsorption of the residual inner aromatic ring B on the catalyst surface would be difficult as a result of steric interference by the two flexible hydroaromatic rings A and C (Fig. 3). The lower rate of hydrogenating the inner ring as compared to the end rings in 1 is reflected in the accumulation of compound 5 in reaction products formed under mild experimental conditions. Slow hydrogenation of B, however, may proceed by a stepwise doublet mechanism, involving slantwise or edgewise adsorption of 5 by means of the sterically unobstructed 9,10-position. Such mechanism would require formation of olefinic intermediates, e.g. 6 and 7, which are indeed found in the reaction products (Fig. 2).

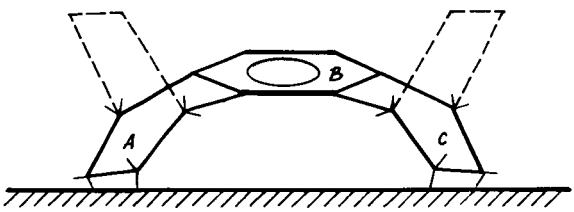

Fig. 3. Steric interference with flatwise adsorption of 1,2,3,4,5,6,7,8-octahydroP(5)

It should be noted that, depending on the surface structure and the strength of adsorption, steric interference of the type indicated in Fig. 3 may not necessarily be equally effective with different types of hydrogenation catalysts. For instance, hydrogenation of 1 using platinum group metals proceeds with strong preference (selectivity ≥75%) for formation of the cis-syn-cis-perhydrophenanthrene stereoisomer (6). This would require (a) preferential flatwise orientation of ring B on the surface; and (b) fast addition of hydrogen from the underside of the adsorbed system, so that all of the four hydrogen atoms found at the asymmetric bridge positions

appear on the same side of the produced hydroaromatic ring. No such selectivity is observed in the present study, viz. the perhydrophenanthrene fraction produced in the presence of sulfided Ni-W/Al_2O_3 consists of a mixture of all six possible stereoisomers in maximal concentrations below 50% of the total fraction. This is in good agreement with the above proposal that in the presence of sulfided catalysts ring B is hydrogenated by a stepwise mechanism, which excludes any possibility of attaining cis-syn-cis stereoselectivity.

To confirm the proposed role of 1,2,3,4-tetrahydroP(3) rather than 9,10-dihydroP(2) as the main first-step intermediate in the process, comparative hydrogenation experiments using these two compounds as feeds were carried out under the following conditions: temperature, 250°C; hydrogen pressure, 1500 psig; and reaction time, 3 hr. It is found that 2 yields considerable amounts (17.2% b.wt.) of phenanthrene, which is then converted to perhydroP(8) via the usual intermediates, e.g. compounds 3 and 5. Significantly, the overall rate of conversion of 2 into 8 is lower compared to that observed in the conversion of phenanthrene into 8 under the same set of conditions. In contrast, 1,2,3,4-tetrahydroP(3) does not undergo any dehydrogenation to phenanthrene under identical conditions, and its relative rate of hydrogenation into 8 is markedly higher than that of phenanthrene proper.

The hydrogenation of pyrene(9) in the presence of sulfided Ni-W/Al_2O_3 was investigated as a function of experimental variables, using an analogous procedure. Figures 4 and 5 summarize the change in product composition from 9 (at 341°C) as a function of hydrogen pressure in the range of 1,000-2,900 psig. As seen, only one type of product containing one hydrogenated ring, i.e. 4,5-dihydropyrene (10), is formed. The yield of this first intermediate decreases with increase in pressure, while that of the preferred second-step hydrogenation intermediate, viz. 1,2,3,3a,4,5-hexahydropyrene (12) passes through a maximum at ∿1,500 psig and then gradually decreases at higher pressure (Fig. 4). It is found that the yield of the alternative second-step product, i.e. 4,5,9,10-tetrahydropyrene (11), is very low in the entire pressure range, indicating that this compound is not an important intermediate in the hydrogenation process. The strong preference for hydrogenation of 10 into 12 rather than into 11 apparently depends on a marked difference in the position of the respective aromatic saturation equilibria. Compound 11 contains two rather strained hydroaromatic rings which should be succeptible to easy dehydrogenation, whereas 12 contains two non-strained hydroaromatic rings in a skewed chair conformation which should be more resistant to dehydrogenation. Figure 5 indicates that hydrogenation of 12 to yield perhydropyrene (14) involves the intermediate formation of 1,2,3,3a,4,5,5a,6,7,8-decahydropyrene (13), followed by slow hydrogenation of the residual tetrasubstituted aromatic ring in 13. Examination of molecular models shows that flatwise adsorption of this residual aromatic ring on the catalyst surface would be difficult due to steric interference by the three surrounding hydroaromatic rings.

The observed slow rate of hydrogenating the inner ring in 1,2,3,4,5,6,7,8-octahydrophenanthrene (5), and the apparent slow rate of hydrogenating the residual tetrasubstituted ring in 1,2,3,3a,4,5,5a,6,7,8-decahydropyrene (13), to yield perhydropyrene (14), indicate that sterically blocked aromatic rings in polycyclic aromatic-naphthenic systems could be markedly resistant to hydrogenation in the presence of sulfided catalysts. This could provide a plausible explanation for the observed resistance of coal-derived liquids to complete hydrogenation, even in case the aromatic saturation equilibria are fully displaced in the direction of saturation (1).

EXPERIMENTAL

Apparatus - An autoclave of 300 ml capacity, rated at 4,000 psi (510°C), was adopted for use as a semi-batch reactor. The autoclave was equipped with a magnetic stirrer, a temperature-controlled heater, a pressure gage, and a water cooling system. It was connected to a high pressure hydrogen source through a check valve and a regulator permitting the maintainance of a constant pressure throughout the experiment.

Catalysts - A wide range of supported Ni-Mo, Ni-W, and Co-Mo systems, obtained

commercially or prepared in this Department, were used in a preliminary screening of hydrotreating catalysts. The selected catalyst had a surface area of 225 m^2/g, and contained NiO, 5.1; WO_3, 20.2; Fe_2O_3, 0.03; and Al_2O_3, 74.1% b.wt. It was sulfided at 300°C and 250 psig with a mixture of hydrogen and carbon disulfide, using an appropriately designed pressure flow system (1).

Procedure - Highly purified samples (> 99%) of phenanthrene and pyrene were used as starting materials. In each experiment were used 13 g of the aromatic compound and 2.6 g of presulfided catalyst. After flushing, the charged autoclave was quickly brought to the desired temperature and hydrogen pressure, and kept under constant conditions for the selected length of time (2 hr in most experiments). At the end of each run, the reaction mixture was rapidly cooled to room temperature, and after releasing the pressure, dissolved in carbon tetrachloride, filtered to remove the catalyst, and analyzed.

Analysis - Products from the hydrogenation reactions were identified by mass spectrometry, PMR analysis, and measurement of gas chromatographic retention volumes. In most cases structures were confirmed by comparison with pure reference compounds. Quantitative analysis of product components was performed by temperature-programmed (60-270°C; 4°C/min) gas chromatography with a 9' x 1/8" column packed with 6% OV-17 on 100-120 mesh Chromosorb W.

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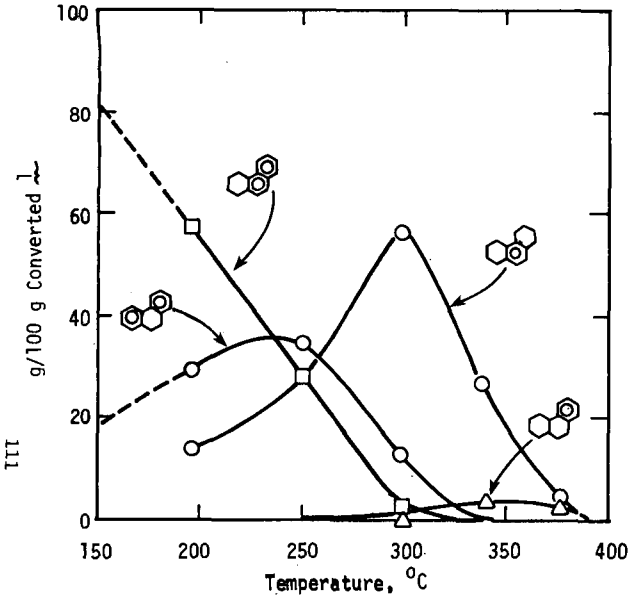

Fig. 1. Change in Product Composition from Hydrogenation of Phenanthrene (1) as a Function of Temperature (Stage A).

Catalyst: Sulfided Ni-W on Alumina

Pressure: 2900 PSIG

Reaction Time: 2 hr

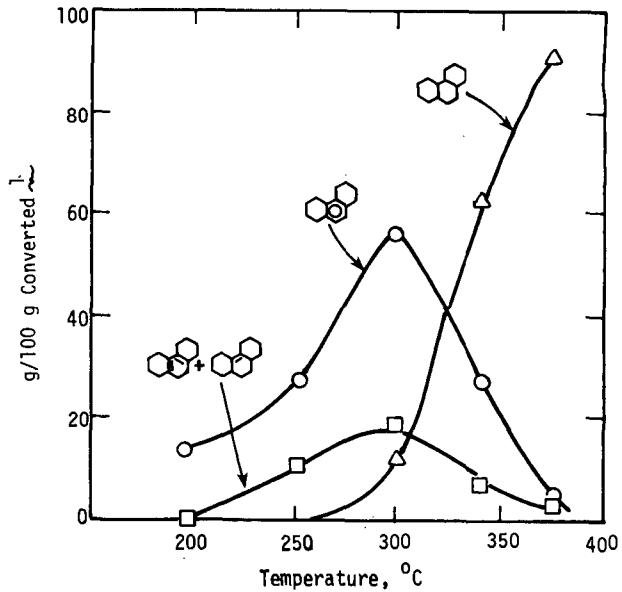

Fig. 2. Change in Product Composition from Hydrogenation of Phenanthrene (1) as a Function of Temperature (Stage B).

Catalyst: Sulfided Ni-W on Alumina

Pressure: 2900 PSIG

Reaction Time: 2 hr

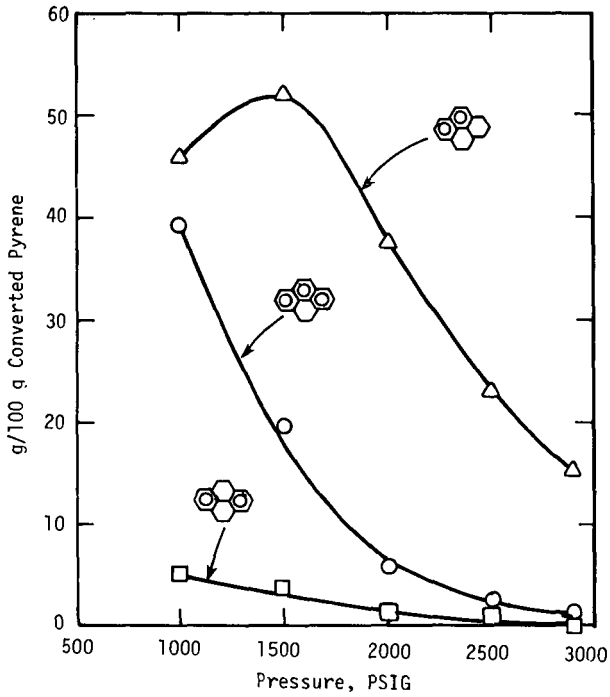

Fig. 4. Change in product composition from hydrogenation of pyrene as a function of pressure (Stage A).
Catalyst: Sulfided Ni-W on Alumina;

Reaction Temperature: 341°C;
Reaction Time: 3 hr.

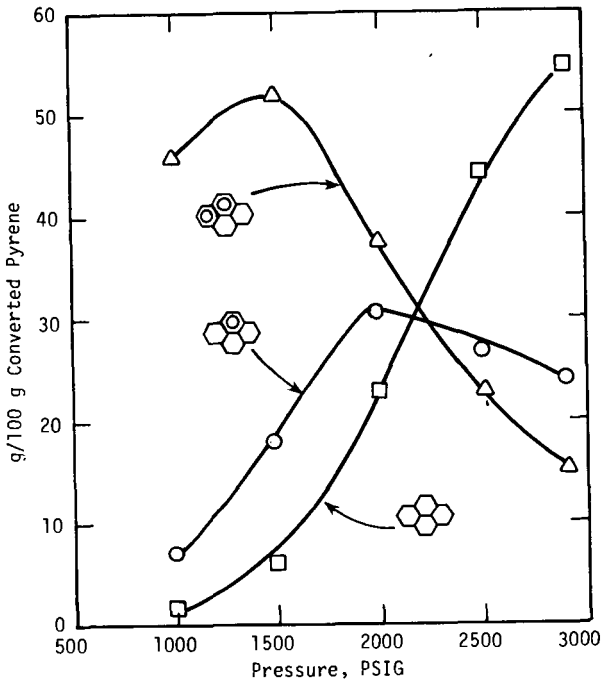

Fig. 5. Change in product composition from hydrogenation of pyrene as a function of pressure (Stage B).
Catalyst: Sulfided Ni-W on Alumina,

Reaction Temperature: 341°C;
Reaction Time: 3 hr.