DOE/PC/89775--6

DE92 003082

CONTROL OF CATALYTIC HYDROTREATING SELECTIVITY WITH AMMONIA

Report for July 1, 1991 to September 30, 1991

Report No.: DOE/PC89775-6

Grant No.: DE-FG22-89PC89775

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Effect of Ammonia on the Hydrogenation of Phenanthrene During the Hydrodenitrogenation of Quinoline

Abstract

The hydrogenation of phenanthrene in the presence of 24 kPa of ammonia was studied during the hydrodenitrogenation (HDN) of quinoline on a sulfided NiMo/Al_2O_3 catalyst at 360°C, 6.9 MPa total H_2 pressure in a vapor phase tubular reactor. Ammonia, through competitive adsorption, reduced the formation of phenanthrene hydrogenated products and the hydrocracking of 9,10-dihydrophenanthrene to biphenyl. The effects occur largely when the HDN reactions are substantially completed.

Introduction

The effect of ammonia on the hydrogenation of naphthalene and butylbenzene during the hydrodenitrogenation (HDN) of quinoline was recently reported.[1] The motivation behind those studies and this study was to investigate the control of hydrogenation selectivity of aromatic hydrocarbons in coal derived liquids by the addition of ammonia during hydrotreating. This study focused on the effect of ammonia on the hydrogenation of phenanthrene as a representative three ring aromatic hydrocarbon.

Limited literature is available on the reactions of phenanthrene. Shabtai et al.[2] reported on the hydrogenation of phenanthrene and pyrene in a semi-batch autoclave reactor. Under their conditions, they found 1,2,3,4-tetrahydrophenanthrene, rather than 9,10-dihydrophenanthrene, to be the main first-step towards the complete hydrogenation of phenanthrene. Lemberton and Guisnet[3] studied phenanthrene hydroconversion and recommended it as a test reaction for studying hydrogenating and cracking properties of coal hydroliquefaction catalysts. In a brief study, LaVopa[4] found that the addition of piperidine restricted the amount of hydrogenation of phenanthrene during its purification by hydrotreatment.

Experimental

The reactor and catalyst used in this study have been described in previous reports.[1,5]

Reactants. All runs were made with feeds consisting of 0.24 mol/L of phenanthrene (99+% pure, Aldrich) and 0.024 mol/L of quinoline (99% pure, American Tokyo Kasei). To achieve the desired solubility of phenanthrene it was necessary to use tetralin (99% pure, Aldrich) as the solvent rather than hexadecane which was the solvent in the earlier related study of the hydrogenation of naphthalene. Propylamine (98% pure, Aldrich) when desired was added at a concentration of 0.24 mol/L to generate *in situ* an ammonia partial pressure of 24 kPa in the reactor. Hydrogen sulfide partial pressure of 12 kPa, for maintaining the sulfided state of the catalyst, was generated *in situ* in the reactor by the addition of 0.12 mol/L of 1-dodecanethiol (98% pure, Aldrich) to the feed.

Analysis. Liquid samples of the reactor effluent were collected downstream from a low-pressure phase separator, and analyzed on a Perkin-Elmer Sigma 1B gas chromatograph equipped with dual flame ionization detectors. Concentrations of the products were related to the starting liquid feed. Carbon mass balances on total products compared to phenanthrene disappearance exceeded 93%. Separation of reaction species was accomplished by using either Supelco SPB-35 (30 meters, 0.25mm ID, 0.25μm) or Supelcowax 10 (30 meters, 0.25mm ID, 0.25 μm) columns. Phenanthrene and 9,10-dihydrophenanthrene were identified by comparing their retention times with those of their pure standards. The presence of other products was identified by GC/MS.

Results

Figure 1 shows a plot of the effect of added ammonia on the solvent, tetralin. There was hydrogenation and dehydrogenation of several percent of tetralin to decalin and naphthalene which was generally unaffected by the presence of 24 kPa of ammonia. The high concentration of tetralin overwhelms the effect of ammonia.

Data were obtained at a range of space-times expressed here relative to phenanthrene. Figure 2 shows a plot of reactant and products for the hydrogenation of phenanthrene with and without ammonia generated *in situ*. Five species of hydrogenated phenanthrenes were detected on the gas chromatograph. Based on GC and GC/MS analyses, the hydrogenated products were identified as 9,10-dihydrophenanthrene (P2H), 1,2,3,4-tetrahydrophenanthrene (P4H), perhydrophenanthrene (PHP), and two species of octahydrophenanthrene (P8H), 1,2,3,4,5,6,7,8-P8H and 1,2,3,4,9,10,11,12-P8H. The two species of P8H were lumped together as one because of poor resolution of their peaks on the GC. Some hydrocracking also occurred, as shown by the formation of biphenyl.

Figure 3 shows a plot of the hydrodenitrogenation of quinoline without added ammonia and in the presence of 24kPa of ammonia. As in the previous studies with naphthalene and butylbenzene, ammonia is seen to have only a slight inhibiting effect on the overall removal of nitrogen from quinoline. Complete HDN was achieved at the highest space time.

The effect of added NH_3 is seen most clearly at the highest space-times. Figure 4 shows that NH_3 suppresses complete hydrogenation to PHP and Figure 5 shows that it reduces cracking of P2H to biphenyl.

Kinetic Model. The most detailed information on the reaction network appears to be that of Shabtai et al.[2] They studied the hydrogenation of phenanthrene over several catalysts, particularly a sulfided NiW/Al_2O_3 at temperatures of 200-380°C and 2900 psig. They concluded that the primary product is P4H while P2H was not an important intermediate in the whole hydrogenation process. P4H is converted to P8H and then PHP. The model used here (Figure 6) basically follows that of Shabtai et al. Moreau and Geneste[6] took phenanthrene as being hydrogenated to either P2H or P4H by parallel pathways, subsequent steps not being specified however. The latter have P2H hydrogenated to P8H whereas our model has assumed that P8H is formed from P4H. Lemberton and Guisnet reported limited studies at 430°C and 10 MPa of hydrogen pressure on a $NiMo/Al_2O_3$ catalyst in which a variety of cracked products were formed as well as various partially hydrogenated products, but no PHP. Assuming that each successive hydrogenating and hydrocracking step in Figure 6 proceeds via first order reaction, then first order rate constants can be calculated for the sets of data with and without added ammonia as shown in Table 1. Figures 7 and 8 show the fit of the first order rate constants.

Table 1 First order rate constants for the hydrogenation of phenanthrene to products.

Added ammonia concentration (kPa)	First order reaction rate constants				
	k_1	k_2	k_3	k_4	k_5
0	0.00405	0.00240	0.00304	0.000290	0.000244
24	0.00403	0.00210	0.00270	0.000103	0.000114

unit of k = (mol of phenanthrene)/(hr g of catalyst)

Discussion

The results can be well interpreted in terms of competitive adsorption effects between phenanthrene and its hydrogenated products on the one hand and quinoline and its nitrogen-containing HDN products and NH_3 on the other. The effect of ammonia on tetralin was negligible largely because of the higher concentration of tetralin. Phenanthrene is readily hydrogenated and considerable formation of partially hydrogenated products occurred even in the presence of quinoline and its nitrogen-products.

The effect of added ammonia is insignificant or minor on the hydrogenation of phenanthrene and intermediates until quinoline and its nitrogen-containing HDN products are largely removed because of the greater adsorptivity of the latter relative to NH_3. Therefore k_1, k_2, and k_3, which represent upstream behavior, shows no significant effect of ammonia. On the other hand k_4 and k_5, which represent downstream behavior when nitrogen-containing hydrocarbons have been effectively eliminated, show the substantial inhibiting effect of NH_3 on hydrocracking and further hydrogenation.

The addition of ammonia has little effect on the overall HDN of quinoline. Thus, NH_3 addition provides an operating region where complete HDN of quinoline can be achieved with reduced formation of hydrogenated phenanthrenes and biphenyl.

Uncontrolled hydrocracking is undesirable as it often reduces yield and causes coking. Cracking is usually associated with acidity, so ammonia can suppress the effects of cracking by neutralizing the acidic sites on the surface of the catalyst. In this case, the added ammonia neutralized the acidic cracking sites responsible for the cracking of P2H to biphenyl.

Acknowledgements

The authors acknowledge the assistance of Anthony Modestino from the MIT Energy Laboratory for his help in GC/MS analysis.

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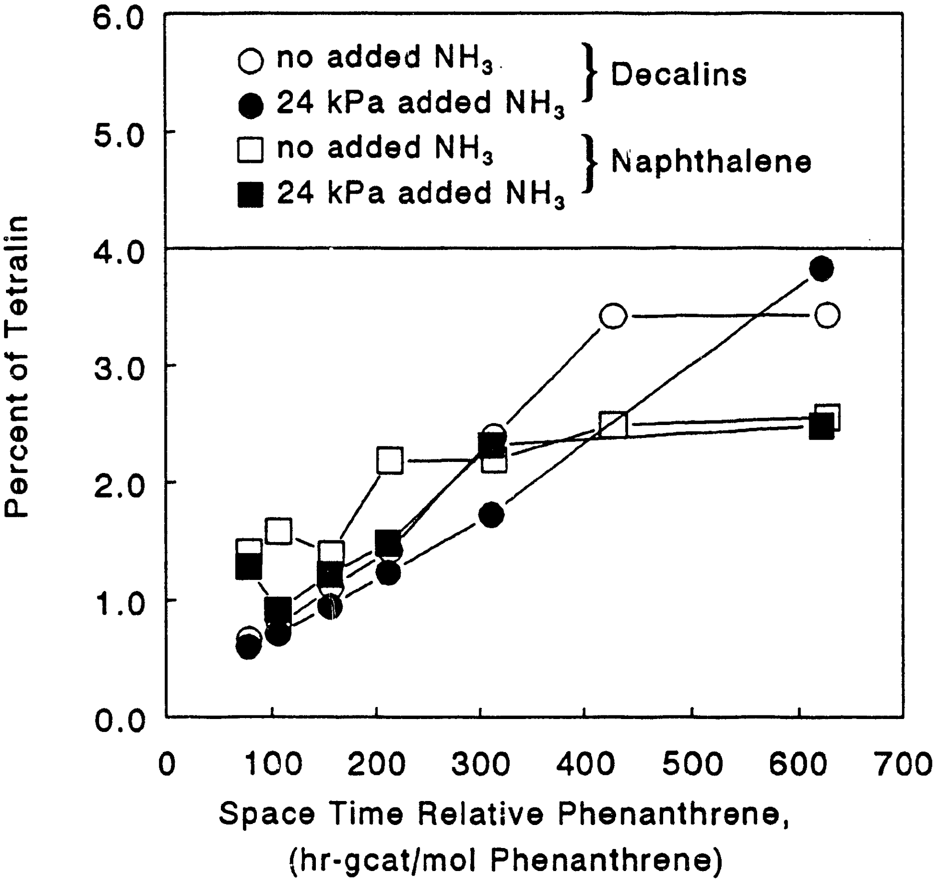

Figure 1 Ammonia had little effect on the hydrogenation of tetralin to decalins or the dehydrogenation of tetralin to naphthalene.

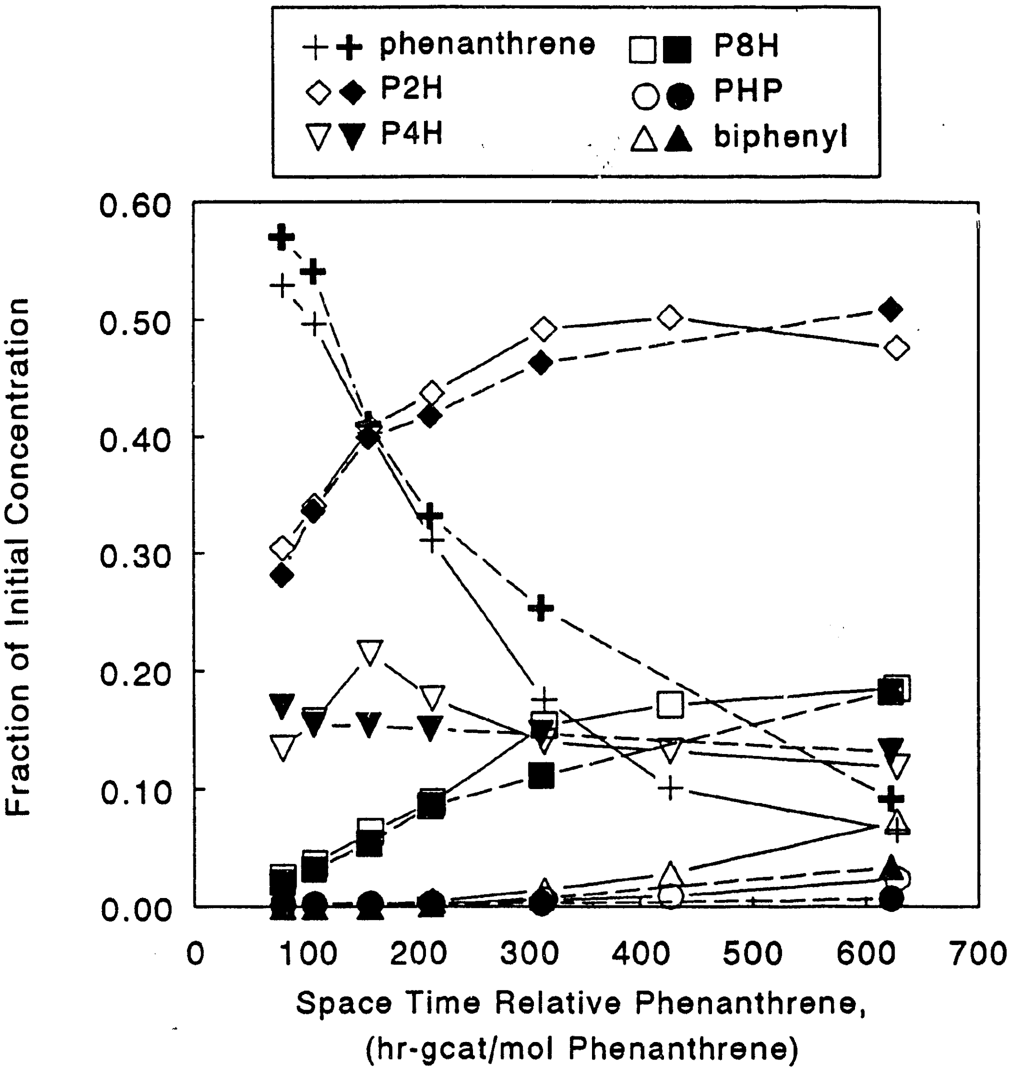

Figure 2 Effect of ammonia on the hydrogenation of phenanthrene during the HDN of quinoline. Open symbols represent no added ammonia; filled symbols represent 24 kPa of added ammonia.

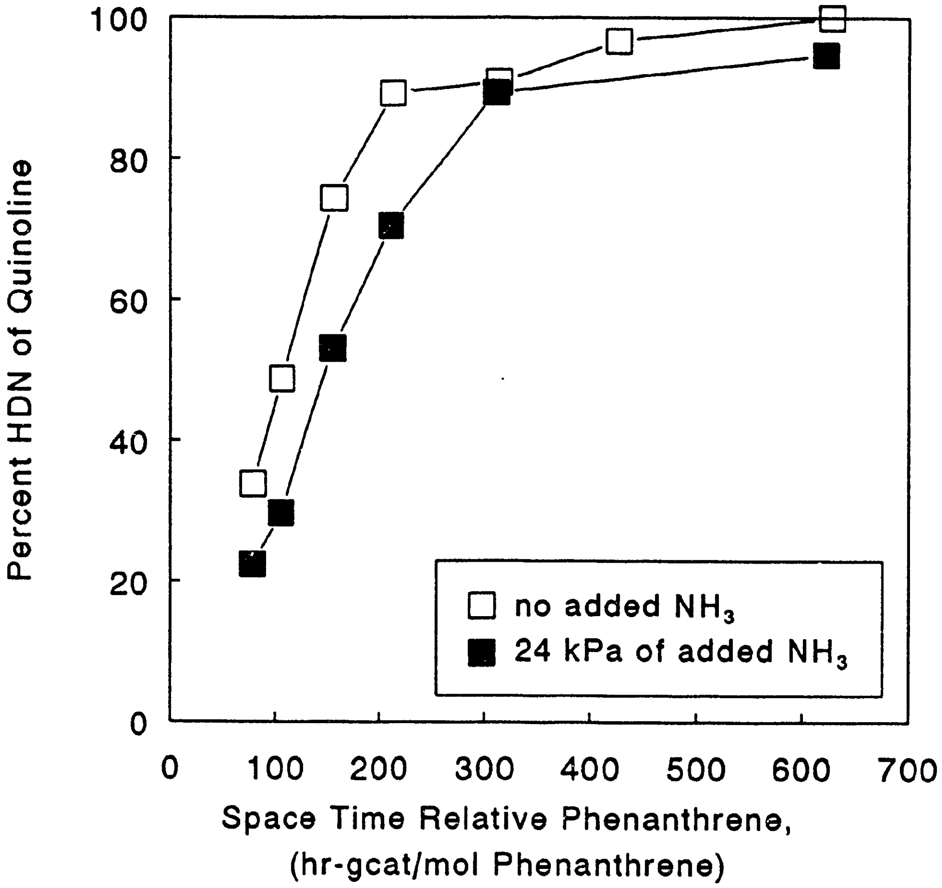

Figure 3 Hydrodenitrogenation of quinoline without added NH_3 and in the presence of 24 kPa of NH_3.

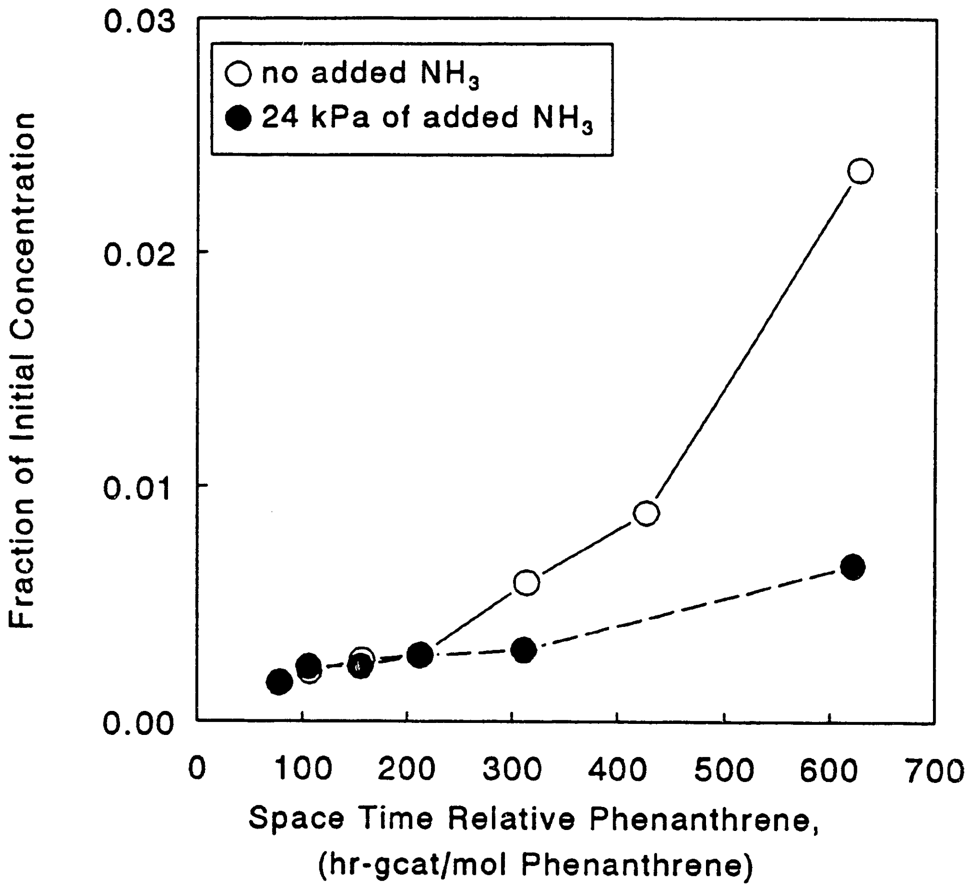

Figure 4 Ammonia inhibits the formation of perhydrophenanthrene.

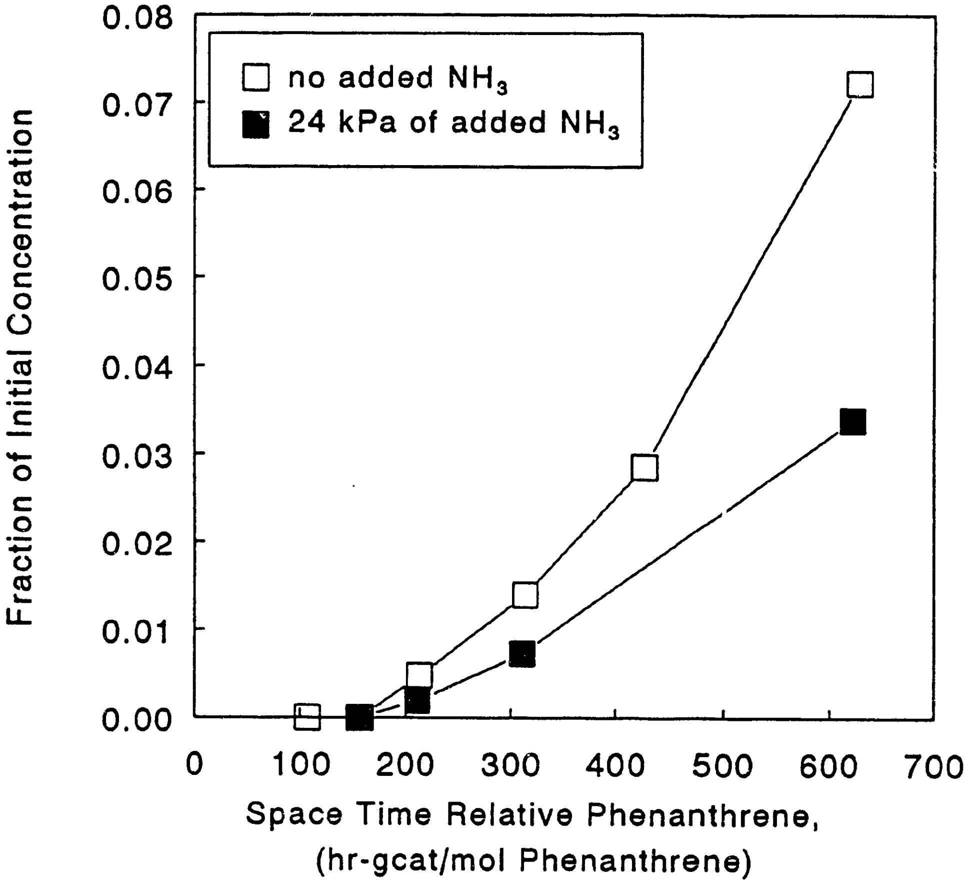

Figure 5 Ammonia reduces the amount of hydrocracking of 9,10-dihydrophenanthrene to biphenyl.

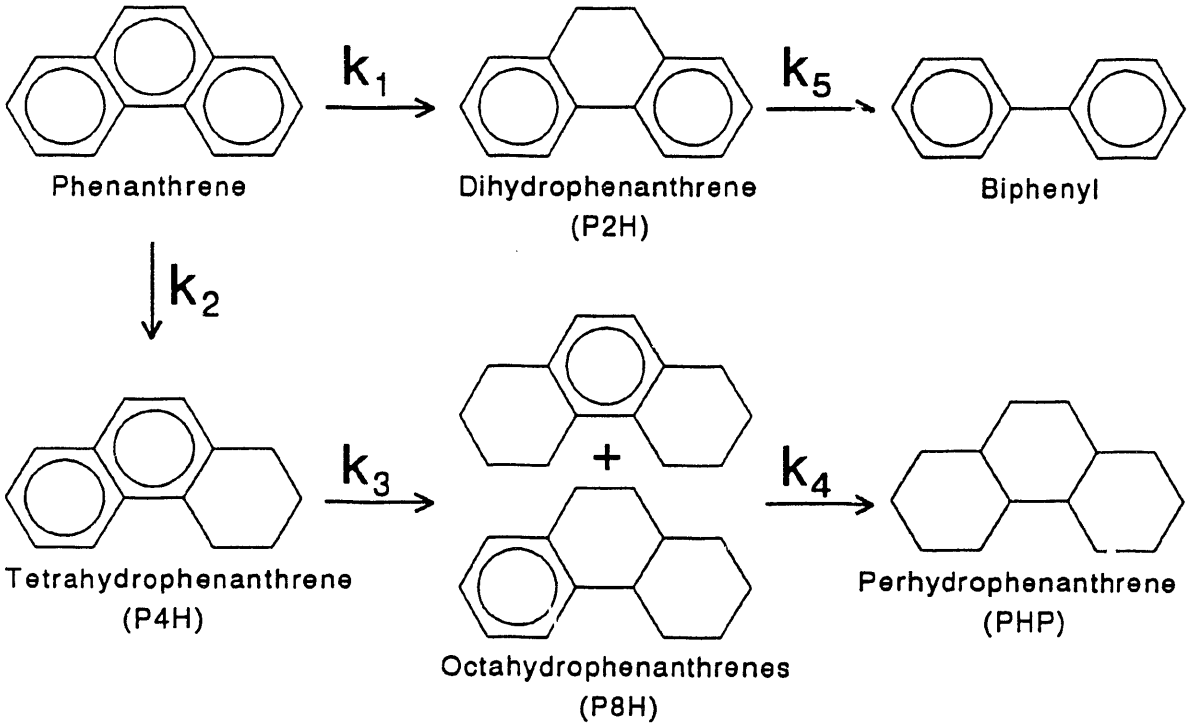

Figure 6 Kinetic model of the hydrogenation of phenanthrene assuming first order reactions.

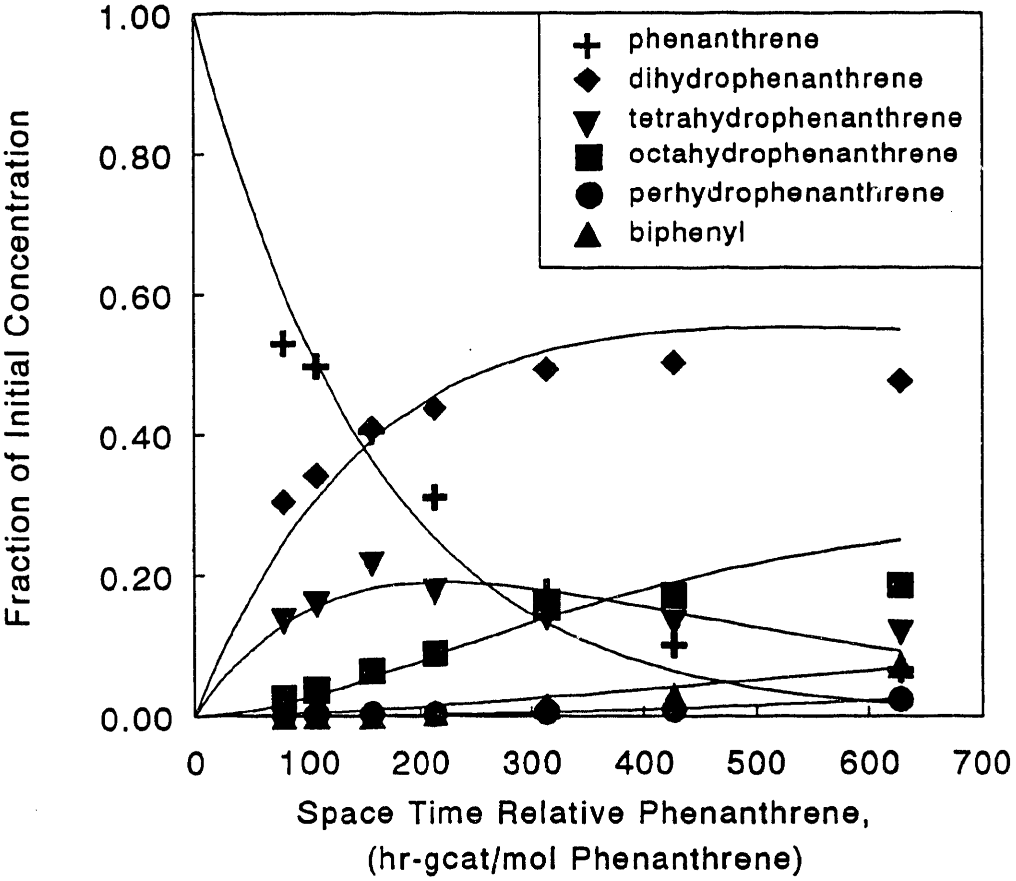

Figure 7 Space time plot of the hydrogenation of phenanthrene with no added ammonia. Solid lines represent first order kinetics.

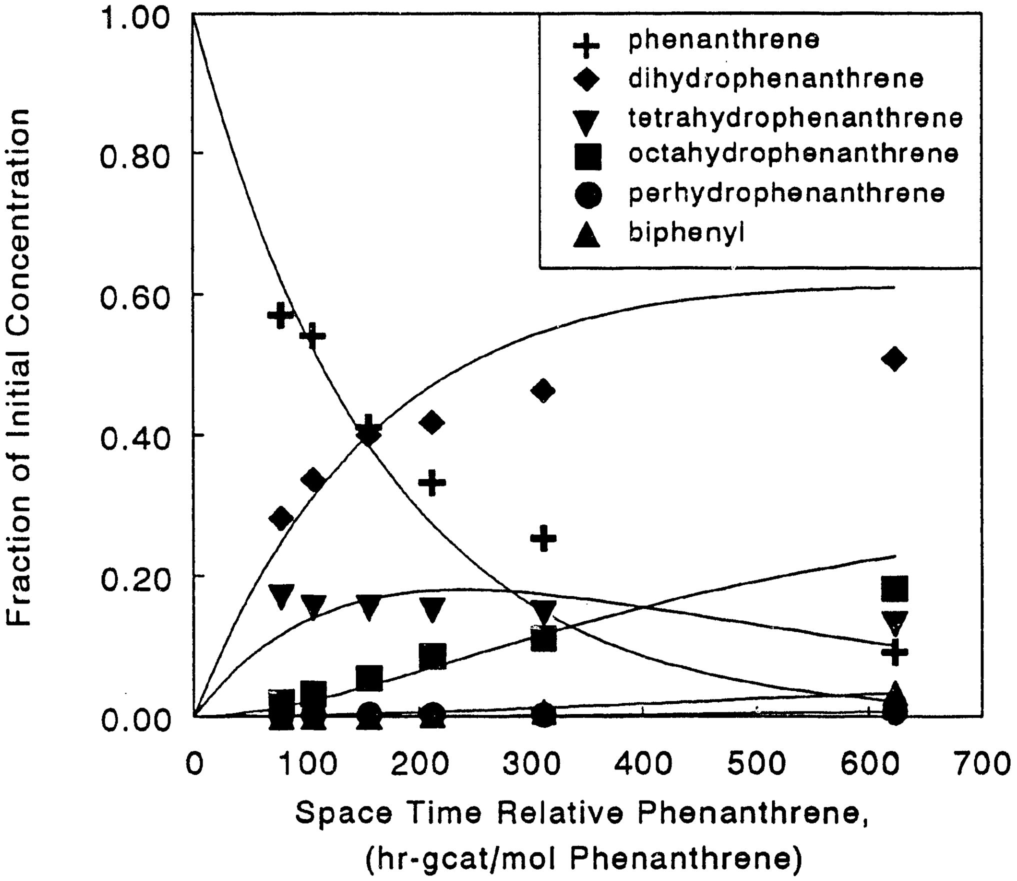

Figure 8 Space time plot of the hydrogenation of phenanthrene with 24 kPa of ammonia. Solid lines represent first order kinetics.

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