THE KINETICS OF CATALYTIC HYDROGENATION OF PYRENE--IMPLICATIONS FOR DIRECT COAL LIQUEFACTION PROCESSING*

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INTRODUCTION

Although recycling heavy solvents has recently re-emerged[1,2,3,4] as a key to cutting the cost of direct coal liquefaction, little data for the hydrogenation of heavy solvent donors have been reported. This study addresses the kinetic and thermodynamic aspects of catalytic hydrogenation of pyrene, a donor solvent precursor thought to play an important role in coal liquefaction processes that use heavy recycle solvents.[5,6]

In the presence of a catalyst, pyrene (Py) is hydrogenated to di- (H_2Py), tetra- (H_4Py), hexa- (H_6Py), deca- ($H_{10}Py$) (Figure 1) and perhydro- ($H_{16}Py$) species via a complex mechanism involving a network of reversible parallel and series reactions. Though several studies have dealt with aspects of pyrene hydrogenation, including hydrocracking reactions,[7] reaction product distributions[8,9] and thermodynamic properties,[10] the kinetics of hydrogenation have not been previously reported.

EXPERIMENTAL

Thirty-six batch hydrogenation experiments were performed with solutions of 9.1 wt % pyrene in n-hexadecane, which approximated the concentrations found in integrated two-stage liquefaction recycle solvents.[11] To evaluate the effects of reaction conditions on the kinetics of hydrogenation, reactions were performed over a range of conditions: Temperatures of 348, 374 and 394°C, pressures of 500, 1250 and 2000 psig, and catalyst/pyrene weight ratios of 0.05, 0.15 and 0.45. Several experiments performed without catalyst confirmed that contributions of homogeneous reactions and reactor wall effects were insignificant. In addition, several catalyzed experiments performed with hexahydropyrene proved the existence of reversible reaction steps.

Materials. Pyrene, hexahydropyrene, and n-hexadecane were used as obtained from Aldrich Chemical Company. Modified Shell 324, a Ni-Mo/alumina catalyst currently used in the second stage of integrated two-stage pilot plant operations,[2] was added to the reactors as a -200 mesh powder. High purity hydrogen (99.999%) was used in all the experiments.

Apparatus and Procedure. The batch reactions were performed in stainless steel microreactors,[12] equipped with thermocouples and pressure transducers, with a liquid capacity of 3.6 cm^3 and a gas volume of 22 cm^3. Four reactors could be operated simultaneously. After the reactors were charged with 100 mg of pyrene, 1 g of n-hexadecane and 5, 15 or 45 mg of catalyst, they were pressurized with hydrogen (420, 1050 or 1850 cold charge), and heated to temperature (time to temperature = 1 min) in a fluidized sand bath while

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being horizontally shaken at 200 cycles/min. Temperatures and pressures were recorded with a digital data acquisition system during the course of the experiments. Following the heating period, the reactor vessels were rapidly quenched to ambient temperature (time of quench = 10 sec), and the products of the experiment were removed for analyses. It was estimated from the reactor heat-up and quench rates that the time at temperature could be determined to within 0.5 min. Temperatures could be maintained constant to within ± 2°C and pressures to within ± 20 psig during the heating period of the experiments.

Product Analyses. The products were washed from the reactor with toluene, filtered to remove catalyst and transferred to a volumetric flask. Following addition of an internal standard (2-methylnaphthalene), the product solution was brought to 50 ml with additional toluene and analyzed by gas chromatography (Hewlett-Packard 5840A with flame ionization detection FID) using the following conditions: 1/8 in x 10 ft column with Supelco 10% SP-2100 on 100/120 Supelcoport, temperature 220°C, nitrogen carrier gas 20 cc/min.

Gas chromatography/mass spectrometry techniques were used to identify the order of elution of components of the reaction mixture, which agreed with previously published results.[9] Quantitative analysis of the reaction mixture was accomplished using external and internal standards. The external standard, a solution of 2-methylnaphthalene, n-hexadecane, pyrene and 1,2,3,6,7,8-hexahydropyrene in toluene was used to obtain FID response factors for the components relative to the internal standard, 2-methylnaphthalene. These were 0.99 for n-hexadecane, 1.10 for hexahydropyrene and 1.04 for pyrene. The relative response for hexahydropyrene was used for the other hydropyrenes. The weights (W) of n-hexadecane, pyrene and hydropyrenes in each sample were calculated from their GC chromatogram areas (A), the response of 2-methylnaphthalene (R_{mn}) and their relative response (R_r).

$$W = R_r \cdot R_{mn} \cdot A$$

The concentration of pyrene and hydropyrenes was calculated on a molal, moles/1000 g hexadecane, basis. Concentration was normalized to initial pyrene concentration for the kinetic calculations.

CALCULATIONS

As a first step in delineating the overall reaction network for catalytic pyrene hydrogenation, the hydrogenation of pyrene to 4,5-dihydropyrene (equation 1) was analyzed:

$$Py + H_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_2Py \qquad (1)$$

The assumption that pyrene is not formed directly from hydropyrenes other than H_2Py and does not directly form hydropyrenes other than H_2Py is supported by reported studies of hydrogenation product distributions as a function of temperature and pressure.[9] Because the hydrogen concentration was in excess during the reactions (e.g., minimum of 26 moles of H_2 per mole Py), the rates can be modelled by pseudo first-order kinetics:

$$\frac{d[Py]_n}{dt} = k_{-1}[H_2Py]_n - k_1[Py]_n \quad (2)$$

$$\frac{d[H_2Py]_n}{dt} = f(t_n) \quad (3)$$

$[Py]_n$, $[H_2Py]_n$ ≡ molar concentrations of pyrene and dihydropyrene respectively, relative to the initial concentration of pyrene after n time intervals.

k_1, k_{-1} ≡ pseudo first-order rate constants.

$f(t_n)$ ≡ an empirical function derived by performing a least squares fit $[H_2Py]$ vs time data using piecewise cubic splines.

The values of k_1 and k_{-1} were determined by performing a minimization on F in equation (4):

$$F = \sum_j \left[\left([Py]_n \Big|_{t_n=t_j} - [Py]_j^* \right)^2 + \left([H_2Py]_n \Big|_{t_n=t_j} - [H_2Py]_j^* \right)^2 \right] \quad (4)$$

$[Py]_j^*$, $[H_2Py]_j^*$ ≡ experimental concentrations at time t_j.

$[Py]_n\Big|_{t_n=t_j}$, $[H_2Py]_n\Big|_{t_n=t_j}$ ≡ calculated concentrations at time t_j.

The values of $[Py]_n$ and $[H_2Py]_n$ were estimated by setting $[Py]_o = [Py]_o^* = 1$ and $[H_2Py]_o = [H_2Py]_o^* = 0$ and numerically integrating equations (2) and (3) using a fourth order Runge-Kutta algorithm.

RESULTS AND DISCUSSION

Qualitative aspects of the kinetics of pyrene hydrogenation may be obtained from curves of concentration vs time, at constant temperature and pressure, for the major species of the system. Figure 2 shows curves at 348°C and 1250 psig for the concentration of pyrene and 4,5-dihydropyrene (H_2Py) and Figure 3 for 4,5,9,10-tetrahydropyrene (H_4Py), 1,2,3,6,7,8-hexahydropyrene (H_6Py) and 1,2,3,3a,4,5-hexahydropyrene (I-H_6Py). As can be seen from the figures, the hydrogenated specie with the largest concentration is H_2Py followed by H_6Py, H_4Py and I-H_6Py. For these experiments, the concentration of deca- and perhydropyrenes was less than 1% of the product mixture.

The kinetics and thermodynamics of the formation of 4,5-dihydropyrene are discussed below with respect to the effect of catalyst/pyrene ratio, hydrogen pressure and temperature.

Catalyst/Pyrene Ratio. Figure 4 shows a plot of k_1 and k_{-1} vs catalyst weight for experiments performed at 348°C and 1250 psig pressure. As can be seen from Figure 4, k_1 for hydrogenation of pyrene and k_{-1} for dehydrogenation of dihydropyrene are proportional to catalyst weight, which is proportional to active surface area.

Hydrogen Pressure. From a plot of k_1 and k_{-1} vs H_2 pressure, Figure 5, it can be seen that while k_1 is linearly proportional to pressure up to 1250 psig, k_{-1} is relatively independent of pressure. This supports the assumption that equation (1) is the only reaction directly involving Py up to pressures of at least 1250 psig. However, the high forward rate constant at 2000 psig may indicate a change in reaction mechanism. In addition to the kinetic parameters, the pressure equilibrium constant and heat of reaction may be calculated for hydrogenation of Py to H_2Py. The pressure equilibrium constant K_p is defined as

$$K_p = \frac{1}{P_{H_2}} \frac{[H_2Py]}{[Py]} = \frac{1}{P_{H_2}} \frac{k_1}{k_{-1}} \qquad (5)$$

where P, the hydrogen partial pressure, is taken as the hydrogen fugacity. Based on the rate constants obtained at 348°C for 3 pressures and 3 catalyst/pyrene ratios, K_p was found to be $7.24 \times 10^{-4} \pm 0.61 \times 10^{-4}$ $psig^{-1}$. From K_p values obtained from the 374 and 394°C data, 4.77×10^{-4} and 3.14×10^{-4} $psig^{-1}$ respectively, the heat of hydrogenation ΔH of pyrene to dihydropyrene can be obtained from a van't Hoff plot shown in Figure 6. The enthalpy of hydrogenation was found to be -15 kcal/mole, which is comparable to values for hydrogenation of other polynuclear aromatics.[13]

Temperature. Figure 7 shows an Arrhenius plot of rate constants k_1 and k_{-1}. The apparent activation energies obtained from Figure 6 for the hydrogenation of pyrene and dehydrogenation of dihydropyrene were found to be 28 and 46 kcal/mole respectively for Shell 324 catalyst. As can be seen from Figure 7, although the forward and reverse rate constants are nearly equal at 348°C, the reverse rate constant is over twice that of the forward rate at 394°C. Therefore, although both reaction rate constants increase with temperature, dehydrogenation is favored over hydrogenation at temperatures above 350°C.

CONCLUSIONS

Ultimate application of this kinetic and thermodynamic data to direct coal liquefaction must take into consideration the conditions imposed by the particular process used. However, two generalizations may be made regarding hydrogen supplied by the dihydropyrene component of donor solvents: (1) Increasing hydrogen partial pressure increases both the rate at which H_2Py is formed and the equilibrium concentration of H_2Py. Therefore, pyrene rehydrogenation should be done at as high a pressure as is cost effective. (2) Although an increase in temperature favors the rate of attainment of equilibrium between Py and H_2Py, the position of the equilibrium is shifted toward pyrene. Temperature must therefore be adjusted to achieve an optimum trade-off between rate of formation and maximum possible concentration of H_2Py.

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FIGURE 1

STRUCTURES FOR PYRENE AND HYDROGENATED PYRENES

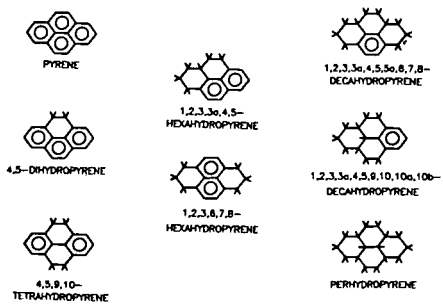


FIGURE 2

CONCENTRATIONS OF PYRENE AND DIHYDROPYRENE
(348 °C, 1250 PSIG, 15 MG SHELL 324)

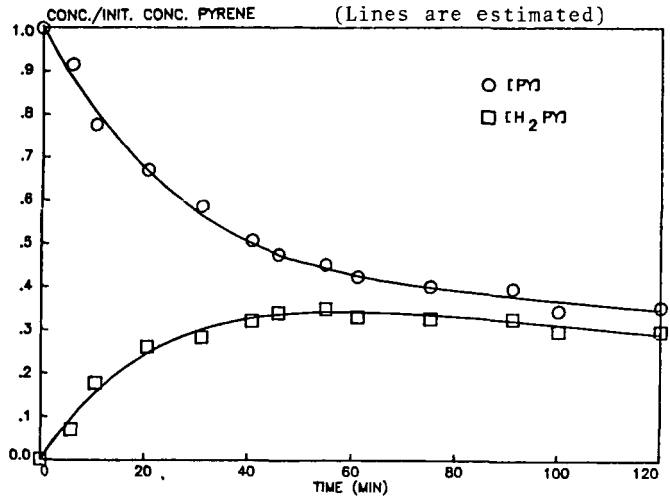


FIGURE 3

CONCENTRATIONS OF TETRA AND HEXA HYDROPYRENES
(348 °C, 1250 PSIG, 15 MG SHELL 324)

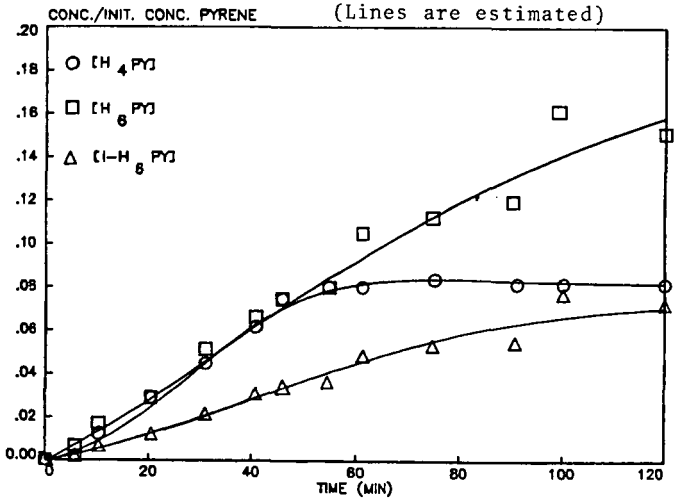


FIGURE 4

DEPENDENCE OF RATE CONSTANTS ON CATALYST LEVEL
(348 °C, 1250 PSIG, SHELL 324)

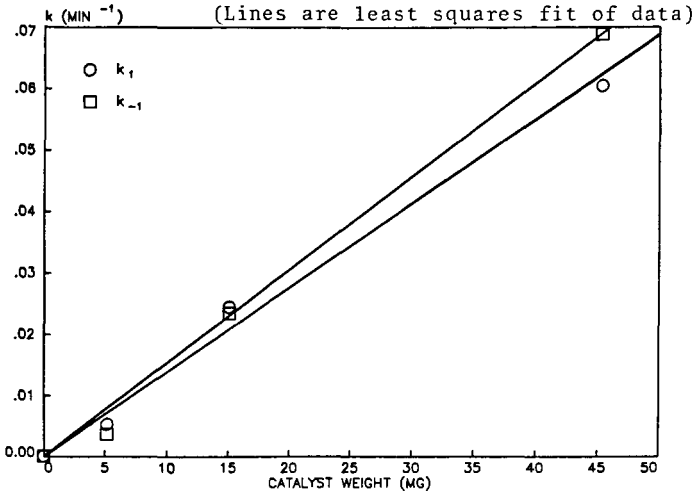


FIGURE 5

DEPENDENCE OF RATE CONSTANTS ON PRESSURE
(348 °C, 15 MG SHELL 324)

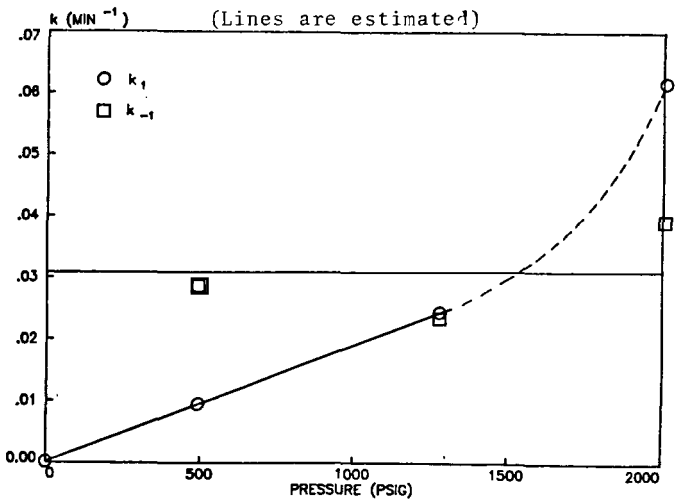


FIGURE 6

ENTHALPY OF HYDROGENATION REACTION
(348 °C, 1250 PSIG, 15 MG SHELL 324)

(Lines are least squares fit of data)

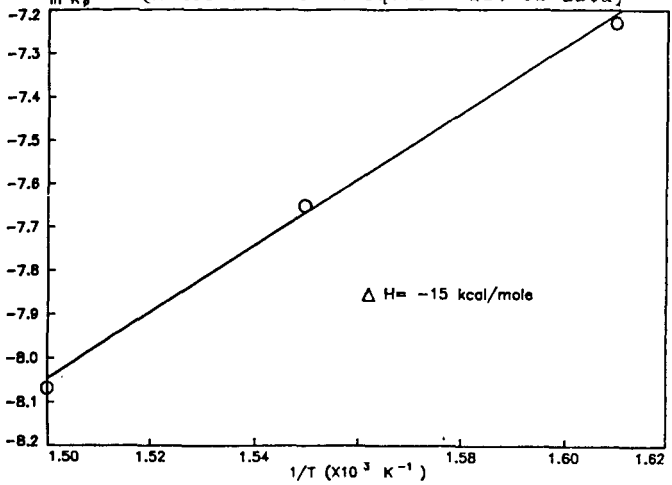
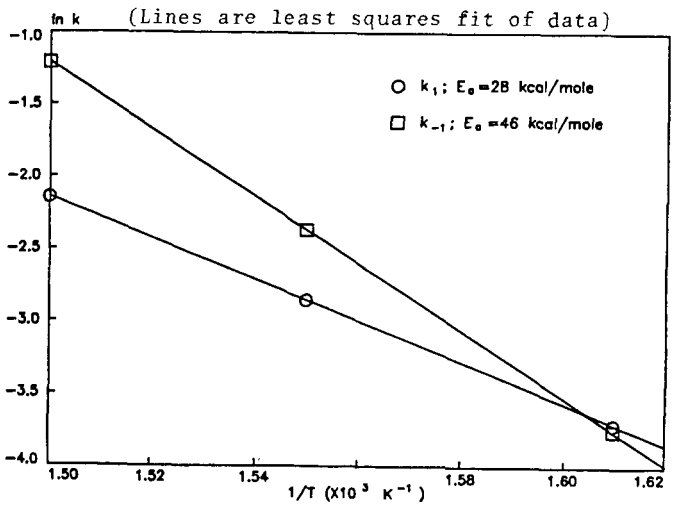


FIGURE 7

ARRHENIUS PLOT OF RATE CONSTANTS
(1250 PSIG, 15 MG SHELL 324)

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