Aromatics Production By Paraffin Dehydrocyclization: Mechanism And The Kinetics Of n-C_8 Dehydrocyclization Reaction On Acidic Pt/Al_2O_3 Catalyst

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The kinetics of n-octane dehydrocyclization reaction has been studied using 0.3% acidic platinum-alumina catalyst in a micro catalytic reactor in a temperature range of 573K - 693K with hydrogen as the carrier gas at 1.8 atmospheric pressure.

A Langmuir-Hishenwood-Hougen-Watson type of rate model was developed for the proposed mechanism involving the aromatization of adsorbed species on the catalyst sites. Sixteen rate equations were derived and the rate equations that gave the best fit of the experimental data were selected.

Consequently, the rate and the thermodynamic constants were evaluated from the model equations developed using a search technique employing the Nelder and Mead modified simplex optimization routine. By using the least squares regression analysis, the activation energies and the heat of adsorption values were evaluated to be 25.465 kcal/gmol and −9.9203 kcal/gmol respectively. The frequency factor was also estimated as 4.896 x 10^8 g mol/(g-catalyst) (h).

Results obtained compared excellently with that of Onukwuli (1988) who obtained a value of 1.516 x 10^8 g mol/(g-catalyst) (h) for the frequency factor and values ranging between 18 – 38 kcal/gmol for the activation energy of normal octane conversion in the temperature range 673 – 733K at a total pressure of 1 atm, using various reactants and H_2 diluents partial pressures. These results are in excellent agreement with the known and expected trends.

1. Introduction
Alkane dehydrocyclization to produce aromatics was first discovered in the late 1930s (Kazanskii and Plate, 1936), and has been a subject of considerable theoretical and industrial importance since that time.

In dehydrocyclization, straight chain hydrocarbons, particularly alkanes are converted to aromatics and hydrogen (IUPAC, 1997). Much of the studies on this subject, involving the paraffins, have been directed towards elucidating the reaction mechanism and not much at quantifying its kinetic parameters.

Dehydrogenation and cyclization of paraffins and cycloparaffins of the corresponding carbon number leads directly to the synthesis of Benzene, Toluene and Xylenes, (BTX) the most important aromatics. In spite of the intense desire to convert alkanes to aromatics, the extent of the study under conditions that approximate commercial reforming conditions is sparse. Normal-octane had been suggested to

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dehydrocyclize to aromatics en-route the classical bifunctional mechanism involving both metal and acid sites, or on metal alone or via a reaction pathway involving dehydrogenation on the metal and cyclization on the acidic support (Gates, Katzer and Schuit, 1979).

The most probable mechanisms for dehydrocyclization reaction on metals are those common to isomerization reactions on metals (Gate, Katzer and Schuit, 1979).

Attempts have been made to explain the role of bifunctional catalyst on naphtha reforming and also to define the rate of conversion of n-heptanes to aromatics by dehydrocyclization (Mills, Heinemann, Milliken and Oblad, 1953; Hettinger, Keith, Gring and Teter, 1955).

Some researchers (Lester, 1969) are of the opinion that the platinum function alone could catalyze aromatics formation by cyclization to a five-carbon ring followed by ring expansion to a six-carbon ring and subsequent dehydrogenation to aromatics. Others contended that direct six-carbon ring formation was the only pathway by which platinum produces significant amount of aromatics (Fogelberg, Gore and Ronby, 1967; Davis and Venuto, 1969).

By using a mechanical mixture of a non-acidic platinum and acidic alumina (Shum, Butt and Sachler, 1984) concluded that the metal function controls dehydrocyclization.

Sivasanker and Padalkar (1988) investigating the dehydrocyclization of hexanes through octanes using Platinum – alumina catalyst concluded that the metal function was the critical parameter with n-hexane and n-heptane; however, both metal function and acid sites could be important for n-octane. Ako and Susu (1993) also investigated the dehydrocyclization of n-octane on both monofunctional and bifunctional platinum-alumina catalysts and observed that the primary products of the dehydrocyclization reaction were ethylbezene and ortho-xylene at temperatures between 593k and 653k.

Callender et al (1973) expressed the view that platinum catalyzed cyclization through C₅ ring closure and that ring expansion led to aromatics. They reported that alumina had activity for cyclization of the alkanes produced from dehydrogenation but that for dispersed platinum, the metal catalyzed cyclization was more rapid.

Heningson (1973) reported that the predominant pathway for the conversion of n-heptane to toluene is via a bifunctional mechanism, and that the acid catalyzed pathway was more rapid.

Dantzenberg and platteeuw (1970) studied the conversion of n-hexane with platinum on a non-acidic alumina catalyst.

They concluded that dehydrocyclization of n-hexane to benzene proceeds along two different reaction paths:

(a) Platinum - catalyzed ring closure whose contribution to total rate of aromatization is proportional to total platinum surface regardless of metal particle size and

(b) Thermal six-ring closure of hexatrienes formed by dehydrogenation from n-hexanes over the platinum function. They argued for a monofunctional reaction pathway for platinum that involves both five and six-ring formation.

Davis (1976) compared the conversion of n-octane at 1 atmospheres and 200 psig and found that the metal catalyzed dehydrocyclizaton selectivity based upon the distribution of C₈ aromatic isomers, was the same at both pressures.

Thus the dominant metal catalyzed cyclization pathway to produce aromatics was 1,6-ring closure provided the support did not have any activity to effect isomerization.

Davis (1983) later proposed that both 1,5 and 1,6-ring cyclization pathways occurred with these catalysts, however at atmospheric pressure the 1,5-cyclization pathway led to the production of C₈-isoalkanes through hydrogenolysis of the cyclopentanes that were formed through 1,5-cyclization.
A bifunctional pathway may form aromatics when acidic alumina support is used. Furthermore, it has been reported that the bifunctional pathway leads to aromatics at least twenty-times faster than the metal pathway only (Davis, 1993). In addition, bifunctional pathway is more selective for aromatics formation than the metal cyclization pathway (Davis, 1993).

There are controversial opinions regarding the exact mechanism of aromatization of alkanes (Ako and Susu, 1986). While the confusions and the doubts as to whether the conversion of alkanes to aromatics on platinum alumina catalysts follow the classical bifunctional mechanism, involving both metal and acid sites ranges on, more work must be done and directed at clarifying and assuaging these doubts Sparks et al (1994).

The objective of the present work therefore was as follows:

1. To study the intrinsic kinetics of the dehydrocyclization reaction of nC₈ using Pt/Al₂O₃ catalyst in a micro catalytic reactor.
2. To derive and establish appropriate mechanistic rate equation for the proposed reaction network.
3. To estimate the kinetics and equilibrium parameters for the best models.
4. To elucidate further, both the mechanism and the roles of the metal and the acidic components of the catalyst.
5. To obtain the activation energies of the dehydrocyclization reaction.
6. To obtain the frequency factors.

5. Construction of the Reaction Network

Reaction path for the dehydrocyclization of n-octane on acidic and non-acidic platinum-alumina catalysts is a complex one. It comprises of several consecutive and simultaneous elementary steps.

Ako and Susu (1993), using the pulse technique, reported that, on the bifunctional platinum-alumina catalyst and in hydrogen carrier gas at the temperature range 563K to 673K, n-octane was converted to i-octane as the sole primary product which in turn was converted to ethylbenzene and ortho-xylene as products throughout the temperature range investigated. The sequences of elementary steps for the scheme above are here presented.
TABLE 1: Mechanism of n-c₈ Dehydrocyclization Reaction on Acidic Platinum-Alumina.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equilibrium Constant</th>
<th>Product</th>
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<tbody>
<tr>
<td>N + S</td>
<td>$k_1$</td>
<td>N.S</td>
</tr>
<tr>
<td>N.S</td>
<td>$k_2$</td>
<td>I.S</td>
</tr>
<tr>
<td>IS + 8S</td>
<td>$k_3$</td>
<td>EB.S + 8H.S</td>
</tr>
<tr>
<td>IS + 8S</td>
<td>$k_4$</td>
<td>OXS + 8H.S</td>
</tr>
<tr>
<td>EBS</td>
<td>$k_5$</td>
<td>PXS</td>
</tr>
<tr>
<td>PXS</td>
<td>$k_6$</td>
<td>MXS</td>
</tr>
<tr>
<td>MXS</td>
<td>$k_7$</td>
<td>OXS</td>
</tr>
<tr>
<td>OXS</td>
<td>$k_8$</td>
<td>EBS</td>
</tr>
<tr>
<td>EBS</td>
<td>$k_9$</td>
<td>MXS</td>
</tr>
<tr>
<td>OXS</td>
<td>$k_{10}$</td>
<td>PXS</td>
</tr>
<tr>
<td>IS</td>
<td>$k_{11}$</td>
<td>I + S</td>
</tr>
<tr>
<td>EBS</td>
<td>$k_{12}$</td>
<td>EB + S</td>
</tr>
<tr>
<td>PXS</td>
<td>$k_{13}$</td>
<td>PX + S</td>
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<td>MXS</td>
<td>$k_{14}$</td>
<td>MX + S</td>
</tr>
<tr>
<td>OXS</td>
<td>$k_{15}$</td>
<td>OX + S</td>
</tr>
<tr>
<td>8HS</td>
<td>$k_{16}$</td>
<td>4H₂ + 8S</td>
</tr>
</tbody>
</table>

The symbols used have the usual meaning, and are listed on page 32. S signifies an empty site while the alphabet-bets with an S at the end refers to absorbed species such that NS and IS stand for absorbed n-octane and absorbed i-octane respectively.
6. The Rate Model Development

The fundamental approach to kinetic analysis of a heterogeneous catalytic reaction involves the postulation of a rate determining step and the formulation of an equation to express the rate in terms of the concentration of the intermediates in that step. (Hougen and Watson, 1943; Froment and Bischoff, 1990; Fogler, 1992 and Satterfield, 1991).

The concentrations of the intermediates must be related to the fluid phase concentrations of the reactants and products (adsorption isotherms).

The simplest theoretical expression for an adsorption isotherm is the Langmuir isotherm, on which the LHHW formalism is based. The underlying assumptions of the Langmuir isotherm includes:

i. Mono layer coverage
ii. Uniformly energetic adsorption sites and
iii. No interaction between adsorbed molecules.

LHHW formalism has been employed in this study to derive the rate laws for the product formation models. In the scheme above, n-octane was first adsorbed on the catalyst site where it was dehydro-isomerized to i-octane. The adsorbed i-octane was then dehydrogenated by aromatization to the two primary products; ethyl-benzene and ortho-xylene, which were then isomerized to other xylenes.

In conventional kinetic analysis, S is considered as an immeasurable quantity and must be related to the measurable entities such as the concentrations or the partial pressures of the reactants as the case may be.

In principle, each of the sixteen elementary steps above could be the rate-determining step. For example, if the adsorption of n-octane is the rate-determining step (reaction 1 of table 1), the rate of the reaction is given by.

\[ r_i = k_i \left( C_N C_S - \frac{C_{NS}}{K_1} \right) \]  

By assuming that other steps are in quasi-equilibrium, the surface coverages NS, IS, MXS, PXS, OXS, EBS and HS can be expressed as follows:

\[ C_{NS} = \frac{C_N C_S}{K_2 K_{11}} \]  \hspace{1cm} (2)

\[ C_{IS} = \frac{C_I C_S}{K_{11}} \]  \hspace{1cm} (3)

\[ C_{EBS} = \frac{C_{EB} C_S}{K_{12}} \]  \hspace{1cm} (4)

\[ C_{PXS} = \frac{C_{PX} C_S}{K_{13}} \]  \hspace{1cm} (5)

\[ C_{MXS} = \frac{C_{MX} C_S}{K_{14}} \]  \hspace{1cm} (6)

\[ C_{OXS} = \frac{C_{OX} C_S}{K_{15}} \]  \hspace{1cm} (7)

\[ C_{HS} = \frac{C_{1/2} C_S}{K_{16}} \]  \hspace{1cm} (8)

A total site balance S as a function of the fluids concentrations of the reactants can be written as

\[ S = \frac{1}{\left( 1 + \frac{1}{K_{11}} \frac{C_I}{C_S} + \frac{C_{MX}}{K_{14}} \frac{C_{MX} C_S}{K_{15}} + \frac{C_{OX}}{K_{15}} \frac{C_{OX} C_S}{K_{15}} \right)} \]  \hspace{1cm} (9)

In this manner equation (1) then becomes

\[ r_i = k_i \left( C_N C_S - \frac{C_{NS}}{K_1} \right) \]  \hspace{1cm} (10)

A summary of the sixteen rate equations obtained in this way is shown in table 2.
TABLE 2: Derived Rate Expressions

1. Adsorption of n-C₈ is rate controlling.
   \[ k_{A} = \frac{C_{n}}{K_{n}} \]

2. Isomerization of adsorbed n-C₈ is rate controlling.
   \[ \tau_{i} = \frac{1 + K_{C_{n}} + K_{C_{n}^{2}}}{C_{n}^{2}} \frac{C_{n}}{K_{n}} \]

3. Aromatization of adsorbed i-C₈ to Ethyl benzene is rate controlling.
   \[ \tau_{a} = \frac{1 + K_{C_{i}} + K_{C_{i}^{2}}}{C_{i}^{2}} \frac{C_{i}}{K_{i}} \]

4. Aromatization of adsorbed i-C₈ to Ortho-xylene is rate controlling.
   \[ \tau_{a} = \frac{1 + K_{C_{i}} + K_{C_{i}^{2}}}{C_{i}^{2}} \frac{C_{i}}{K_{i}} \]

5. Isomerization of adsorbed EB adsorbed Paraxylene is rate controlling.
   \[ \tau_{i} = \frac{1 + K_{C_{i}} + K_{C_{i}^{2}}}{C_{i}^{2}} \frac{C_{i}}{K_{i}} \]

6. Isomerization of adsorbed Meta-xylene to adsorbed Ortho-xylene is rate controlling.
   \[ \tau_{i} = \frac{1 + K_{C_{m}} + K_{C_{m}^{2}}}{C_{m}^{2}} \frac{C_{m}}{K_{m}} \]

7. Isomerization of adsorbed M-xylene to adsorbed O-xylene is rate controlling.
   \[ \tau_{i} = \frac{1 + K_{C_{m}} + K_{C_{m}^{2}}}{C_{m}^{2}} \frac{C_{m}}{K_{m}} \]

8. Isomerization of adsorbed O-xylene to adsorbed EB is rate controlling.
   \[ \tau_{i} = \frac{1 + K_{C_{o}} + K_{C_{o}^{2}}}{C_{o}^{2}} \frac{C_{o}}{K_{o}} \]

9. Isomerization of adsorbed EB to adsorbed M-xylene is rate controlling.
   \[ \tau_{i} = \frac{1 + K_{C_{e}} + K_{C_{e}^{2}}}{C_{e}^{2}} \frac{C_{e}}{K_{e}} \]

10. Isomerization of adsorbed O-xylene to adsorbed P-xylene is rate controlling.
    \[ \tau_{i} = \frac{1 + K_{C_{o}} + K_{C_{o}^{2}}}{C_{o}^{2}} \frac{C_{o}}{K_{o}} \]

11. Desorption of adsorbed i-C₈ is rate controlling.
    \[ \tau_{d} = \frac{1 + K_{C_{i}} + K_{C_{i}^{2}}}{C_{i}^{2}} \frac{C_{i}}{K_{i}} \]

12. Desorption of adsorbed EB is rate controlling.
    \[ \tau_{d} = \frac{1 + K_{C_{e}} + K_{C_{e}^{2}}}{C_{e}^{2}} \frac{C_{e}}{K_{e}} \]

13. Desorption of adsorbed P-xylene is rate controlling.
    \[ \tau_{d} = \frac{1 + K_{C_{o}} + K_{C_{o}^{2}}}{C_{o}^{2}} \frac{C_{o}}{K_{o}} \]

14. Desorption of adsorbed M-xylene is rate controlling.
    \[ \tau_{d} = \frac{1 + K_{C_{m}} + K_{C_{m}^{2}}}{C_{m}^{2}} \frac{C_{m}}{K_{m}} \]

15. Desorption of adsorbed O-xylene is rate controlling.
    \[ \tau_{d} = \frac{1 + K_{C_{o}} + K_{C_{o}^{2}}}{C_{o}^{2}} \frac{C_{o}}{K_{o}} \]

16. Desorption of adsorbed Hydrogen is rate controlling.
    \[ \tau_{d} = \frac{1 + K_{C_{h}} + K_{C_{h}^{2}}}{C_{h}^{2}} \frac{C_{h}}{K_{h}} \]
For this purpose, sixteen rate equations were derived and the rate equations that gave the best fit of the experimental data were selected. The lists of equations considered are as presented in Table 2.

7. Parameter Estimation And Model Discrimination

The experimental data of Ako and Susu (1993) was analyzed, using the equation

\[ F = \sum_{j=1}^{N} |R_{Aj} - \frac{\sum_{j} \Phi}{N}| \]  

(11)

Where \( F \) is the objective function to be minimized and representing the sums of squares of the difference between the observed and predicted rates and \( N \) is the number of experimental data. The parameter estimates were obtained by minimizing the objective function \( F \) using the Nelder and Mead’s modified simplex optimization routine.

The values of the rate parameters and the residuals (\( \Phi_{mn} \)) are presented in Tables 3 and 4. Discrimination among the models was based on the positive ness of the rate and the equilibrium constants, the goodness of fit, and the increase of rate constants with temperature.

8. Discussion of Results

It was discovered that only six of the sixteen derived rate equations shown in Table 2, were found to explain the experimental data. These are the ones based on the following elementary reactions as the rate determining steps:

(i) Adsorption of nC\(_8\) (\( r_1 \)).
(ii) Conversion of adsorbed nC\(_8\) to adsorbed i-C\(_8\) (\( r_2 \)).
(iii) Conversion of adsorbed i-C\(_8\) to adsorbed ethyl-benzene (\( r_3 \)).
(iv) Conversion of adsorbed i-C\(_8\) to adsorbed ortho-xylene (\( r_4 \)).
(v) Desorption of adsorbed meta-xylene (\( r_{14} \)).
(vi) Desorption of adsorbed hydrogen (\( r_{16} \)).

Although the six steps enumerated above were found to predict the experimental data, it is however known that the dehydrogenation of n-C\(_8\) to adsorbed i-C\(_8\) and desorption steps are rather fast relative to other elementary steps in the sequence on the bifunctional catalyst. These models were therefore discarded. Tables 3 and 4. Lists the predicted kinetics and equilibrium parameters for the two models retained.

The temperature dependence of the rate constants is as shown in Figures 2 3,4 and 5 from which the activation energies were calculated for models \( r_3 \) and \( r_4 \) as 25.465kcal/gmol and 22.89 kcal/gmol respectively.

The adsorption coefficients obtained for the model 3 showed the usually expected trend of decrease in the values of adsorption coefficients with temperature while an unexpected trend was noted in model 4. For this reason model 4 was also screened out along with others and model 3 retained as the rate determining step and the best model for representing the kinetics of normal octane dehydrocyclization reaction on acidic platinum-alumina.

The heats of adsorption as calculated from the Arrhenius plots of lnK vs. \( T^{-1} \) were found to be –9.9203 kcal/gmol and 23.307 kcal/gmol for models \( r_3 \) and \( r_4 \) respectively.

These results are in excellent agreement with that of Onukwuli (1988) who has obtained a value of 1.516 x 10\(^8\) gmol/(g-catalyst)(h) for the frequency factor and values ranging between 18 – 38 kcal/gmol for the activation energy of normal octane conversion in a Berty CSTR in the temperature range 673 – 733K at a total pressure of 1atm, using various reactants and H\(_2\) diluents partial pressures.
Table 3: Model parameters for rate equation (3) in table 2.

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<tr>
<th></th>
<th>573K</th>
<th>593K</th>
<th>613K</th>
<th>633K</th>
<th>653K</th>
<th>673K</th>
<th>( \Phi_{\text{min}} )</th>
<th>( A ) gmol/(g-catalyst) (h)</th>
<th>( \Delta E, \Delta H ) kcal/gmol</th>
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<tr>
<td>( k_1 )</td>
<td>0.1357</td>
<td>0.1605</td>
<td>0.1892</td>
<td>1.5717</td>
<td>1.6818</td>
<td>2.2940</td>
<td>4.90E+8</td>
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<tr>
<td>( K_{11} )</td>
<td>2.2350</td>
<td>2.1228</td>
<td>2.0616</td>
<td>1.9148</td>
<td>1.5571</td>
<td>1.8499</td>
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<tr>
<td>( K_3 )</td>
<td>1.6441</td>
<td>1.2822</td>
<td>1.1608</td>
<td>0.8965</td>
<td>0.6415</td>
<td>0.4234</td>
<td>2.95E-4</td>
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<td>( K_{15} )</td>
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<td>0.0624</td>
<td>0.0318</td>
<td>0.0268</td>
<td>0.3541</td>
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<td>( K_{12} )</td>
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<td>( K_{13} )</td>
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<td>( K_{14} )</td>
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<td>( K_{16} )</td>
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Table 4: Model parameters for rate equation (4) in table 2.

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<th></th>
<th>573K</th>
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<th>673K</th>
<th>( \Phi_{\text{min}} )</th>
<th>( A ) gmol/(g-catalyst) (h)</th>
<th>( \Delta E, \Delta H ) kcal/gmol</th>
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<tr>
<td>( k_4 )</td>
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<td>0.84266</td>
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<tr>
<td>( K_{11} )</td>
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<td>0.21748</td>
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<tr>
<td>( K_2 )</td>
<td>0.01986</td>
<td>0.01256</td>
<td>1.3534</td>
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<td>0.2012</td>
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<tr>
<td>( K_{12} )</td>
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<td>( K_{13} )</td>
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<tr>
<td>( K_{14} )</td>
<td>5.356</td>
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<td>( K_{15} )</td>
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<tr>
<td>( K_{16} )</td>
<td>4.8573</td>
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<td>0.15213</td>
<td>10.384</td>
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FIGURE 2: Arrhenius plot using rate constants for model 3

FIGURE 3: Arrhenius plot using equilibrium constants for model 3
FIGURE 4: Arrhenius plot using rate constants for model 4

FIGURE 5: Arrhenius plot using equilibrium constants for model 4
9. Conclusion

The kinetics of n-octane dehydrocyclization reactions using 0.3% commercial Platinum – alumina catalyst has been studied in a micro catalytic reactor over a temperature range 573 – 763 K with hydrogen as carrier gas at 1.8 atmospheric pressure using the pulse technique.

It was found that the rate of dehydrocyclization of n-octane on acidic catalyst was correctly predicted by the model equation involving the rate of aromatization of adsorbed i-octane to ethyl benzene, model $r_3$, which is the best model for representing the kinetics of normal octane dehydrocyclization reaction on acidic platinum - alumina.

The heat of adsorption and the activation energy for the choice model, as calculated from the Arrhenius plots of lnK vs. $T^{-1}$ and lnk vs. $T^{-1}$ were found to be $-9.9203$ kcal/gmol and $25.465$ kcal/gmol respectively. The frequency factor was also estimated as $4.896 \times 10^8$ gmol/(g-catalyst)(h).

These results are in excellent agreement with that of Onukwuli (1988) who obtained a value of $1.516 \times 10^8$ gmol/(g-catalyst)(h) for the frequency factor and values ranging between 18–38 kcal/gmol for the activation energy of normal octane conversion in a Berty CSTR in the temperature range 673 – 733 K at a total pressure of 1 atm, using various reactants and H$_2$ diluents partial pressures.

SYMBOLS USED

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>H</td>
<td>Hydrogen</td>
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<tr>
<td>HS</td>
<td>Adsorbed Hydrogen</td>
</tr>
<tr>
<td>ΔE</td>
<td>Activation Energy, kcal/gmol</td>
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<tr>
<td>ΔH</td>
<td>Adsorption Energy, kcal/gmol</td>
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<tr>
<td>$C_N$</td>
<td>Concentration of normal octane, kmol/cm$^3$</td>
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<tr>
<td>$K$</td>
<td>Adsorption equilibrium constant, atm$^{-1}$</td>
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<td>$A$</td>
<td>Frequency factor, gmol/(g-catalyst)(h)</td>
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<td>$R$</td>
<td>Gas constant, kcal/(gmol)(°K)</td>
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<tr>
<td>$k$</td>
<td>Rate constant, g . mol/(h) (g-catalyst) (atm)</td>
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<td>$T$</td>
<td>Absolute temperature, °K</td>
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<tr>
<td>$W$</td>
<td>Catalyst weight, g</td>
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<td>$F$</td>
<td>Objective function to be minimized</td>
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<tr>
<td>$R_{Ai}'$</td>
<td>Predicted experimental rates</td>
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Greek Letters

<table>
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<td>$\Phi_{min}$</td>
<td>Parameter defined by equation 11.</td>
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References


