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ORIGINAL RESEARCH ARTICLE

KINETIC MODELING OF ETHYLBENZENE ISOMERIZATION USING BODENSTEIN APPROXIMATION TECHNIQUE

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ABSTRACT

Ethylbenzene isomerization reaction is a significant reaction employed in the production of xylene isomers which are used as petrochemical feedstocks. The reaction which proceeds over Pt/Al_2O_3 catalyst is multi-pathway and multi-cycle in topology. Kinetic model for the reaction was developed in this study using the general rate equation approach. Bodenstein approximation, cross-to-square, and Y-to-delta transformation techniques were used to reduce the complex reaction network to a single cycle network. In addition, the general rate equation for reduced single cycle networks was applied to derive the model for the reaction. The Nelder-Mead simplex optimization technique was used to estimate the kinetic parameters in the model. The structure of the model developed indicates that the model reasonably represents the mechanism of the reaction although few anomalies were observed in the values of the kinetic parameters estimated. The activation energy obtained for the rate constants follows the expected trend for multi-step reactions.

1.0 Introduction

Ethylbenzene isomerization is an industrial reaction that is vital in industries that need petrochemical feedstocks. Products of this reaction are precursors to some very important polymer materials. A kinetic model of this reaction is handy when it comes to reactor design, optimization, operations and possible troubleshooting. Kinetic models developed for reactions of industrial importance are usually either empirical in nature or assume some rate-limiting steps (Kangas et al., 2008; Al-Khattaf et al., 2009; Waziri and Al-Khattaf, 2009; Farahani et al, 2020). The power rate-law type of equations usually used to study kinetic behaviors of complex reactions do not usually capture the multiple molecular events involved in such catalytic reactions and, therefore, cannot completely and reliably predict kinetic behavior of such systems. Consequently, models developed via these schemes are usually not reliable for direct scale-up purposes (Helfferich, 2004). Direct large scale-up of industrially significant reactions on the other hand need effective and reliable fundamental kinetic models reflecting the kinetics of the multi-step catalytic pathways of the reaction mechanism.

An earlier study on isomerization of ethylbenzene on bifunctional Pt/Al_2O_3 and Pt-zeolite catalysts was investigated by Robschlager and Christoffel (1979). Their investigation showed that xylenes were produced over the Pt/Al_2O_3 catalyst via the route corresponding to prediction from a bifunctional mechanism in which skeletal rearrangements of tertiary carbocations only were considered to be the rate-determining steps. A systematic methodology to the elucidation of

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reaction networks with multiple numbers of steps and location of nodes was presented in Helfferich (1989). General equations for rate of reactions and yield ratio were developed with a view to elucidate complex reaction networks. Findings from the study indicate that the procedure used is handy in model development and discrimination applications. A kinetic modeling technique that simplifies complex reaction network by employing Bodenstein approximation for trace level intermediates was reported in Chern and Helfferich (1990). The technique reduces complex networks in topology to networks with only pseudo-single steps between nodes; the simpler networks are then used to derive rate expressions for the reactants and products in the network. Fernendes et al. (1998) studied the hydroisomerization of ethylbenzene on Mordenite-based bifunctional catalysts with different platinum contents. The study concluded that hydroisomerization of ethylbenzene is affected by reactant diffusion inside zeolite pores in addition to zeolite acidity and that platinum content affected xylene selectivity due to the formation of hydrogenated intermediates. The concept of Bodenstein approximation and network reduction technique was extended to the modeling of single-cycle reaction network as reported in Chern (2000). Results presented in the study indicated that general rate equations derived is applicable to heterogeneous catalytic reactions involving first-order reactions with respect to intermediates formed in the reaction. Al-Zahrani *et al* (2002) studied the kinetics of transalkylation and isomerization of ortho diethylbenzene using trifluoromethane acid as a catalyst. The work tested power-law type model for transalkylation and disproportionation reaction and findings show that isomerization reaction follow first-order mechanism. Chen and Chern (2003) in their work titled the general rate equation and their application for catalytic reaction networks: pyramidal systems; systematically developed a general rate equation formula that can be used for fundamental kinetic modeling of complex reaction networks that have multi-pathways and multi-intersections. Their work seeks to cover reaction networks not captured by formulas and procedures presented by Chen and Chern (2002a) and Chen and Chern (2002b). The work by Chen and Chern (2009), discrimination of kinetic models for isomerization of n-butene to isobutene, presented the exploitation of analysis of mathematics of multi-step reactions to discriminate between rival mechanisms. The kinetic modeling of non-simple networks was reported in a work by Chern *et al.* (2014). Their study provided an extension to earlier techniques reported to include networks with branches from loops and non-simple networks. Oliveira *et al.* (2016) presented a review of kinetic modeling methodologies for complex processes and the paper analyzed in length advanced kinetic modeling strategies. Farahani *et al.* (2020) studied ethylbenzene/Xylene mixture isomerization over HZSM-5 zeolites catalyst. They developed a kinetic model that considers chemisorption, surface reaction, and diffusional processes for the reaction. Their findings provided an insight on the activation energy for the surface reaction of ethylbenzene into m-xylene.

Considering the significance of general rate equation approach and the limitations of the nature of kinetic studies hitherto practiced, the algorithm of general rate equation was used to model the isomerization of ethylbenzene in this study. The study focused on developing a reliable and effective fundamental kinetic model for the isomerization of ethylbenzene over Pt/ Al_2O_3 catalyst using Bodenstein approximation technique on trace level intermediates.

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2. Methodology

The Bodenstein approximation of trace-level intermediates was the tool used in this work to reduce multi-step reaction networks to reactions with only pseudo-single steps between network nodes and end members. The net rate contribution of a multi-step network segment between nodes X_j and X_k represented by the reaction pathway below is given in equation 1 (Chern and Helfferich, 1990).

$$X_j \leftrightarrow X_{j+1} \leftrightarrow \ldots \leftrightarrow X_{j+i} \leftrightarrow \ldots \leftrightarrow X_k$$

$$r_{j\to k} = \Lambda_{jk}\left[X_j\right] - \Lambda_{kj}\left[X_k\right] \qquad 1$$

The segment coefficients (Λ) for the reaction pathway presented above are evaluated using equations 2 and 3.

$$\Lambda_{jk} = \frac{\prod_{i=j}^{i=k-1} \lambda_{i,i+1}}{D_{jk}} \qquad 2$$

$$\Lambda_{kj} = \frac{\prod_{i=j}^{i=k-1} \lambda_{i+1,i}}{D_{jk}} \qquad 3$$

Where λ represents the pseudo-first order rate coefficients of quasi-single molecular steps and are also the products of the actual rate coefficients and the concentration of any co-reactants of the respective steps (Chern and Helfferich, 1990). The numerators of the segment coefficient expressions given in equation 2 and 3 are the products of the forward rate coefficients and reverse rate coefficients in the pathway respectively. The operator D_{jk} is evaluated using equation 4.

$$D_{jk} = \sum_{i=j+1}^{k}\left(\prod_{m=j+1}^{i-1} \lambda_{m,m-1} \prod_{m=1}^{k-1} \lambda_{m,m+1}\right) \qquad 4$$

A loop coefficient is used to reduce parallel pathways in a network into a single lumped pathway. The expressions for forward and reverse loop coefficients are shown in equation 5 and 6 (Chen and Chern, 2009).

$$L_{ij} = \sum_{k=1}^{m} \Lambda_{ij}^{(k)} \qquad 5$$

$$L_{ji} = \sum_{k=1}^{m} \Lambda_{ji}^{(k)} \qquad 6$$

Collective coefficients (Γ_{ij}) are used to group segment rate coefficients in a network segment so as to reduce network portions with higher number of coefficients to a pseudo-single step.

2.1 Reaction Mechanism and Network

The mechanism of the reaction is presented below:

$$\mathrm{EB} + \mathrm{S} \rightleftharpoons EBS$$

$$\mathrm{EBS} \rightleftharpoons OXS$$

$$OXS \rightleftharpoons PXS$$
$$PXS \rightleftharpoons MXS$$
$$MXS \rightleftharpoons EBS$$
$$OXS \rightleftharpoons OX + S$$
$$PXS \rightleftharpoons PX + S$$
$$MXS \rightleftharpoons MX + S$$

The reaction network and steps involved in reduction of the complex network into a single-cycle network for modeling is presented in steps 1-8 below:

1. The network depicting the mechanism for the reaction showing multi-pathways and multi-intersections is shown in Figure 1.

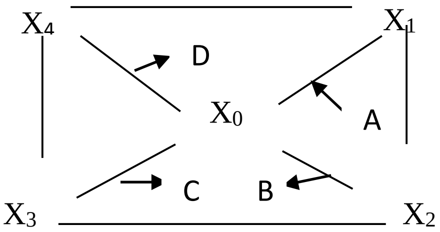

Figure 1: Reaction network for the four-node pyramidal isomerization reaction.

2. The network in Figure 1 can be viewed as pyramidal network with four nodes in the base triangle. The four nodes being X_1, X_0, $X_{3,}$ and X_4. The pyramidal network with the four nodes in the base triangle is shown in Figure 2.

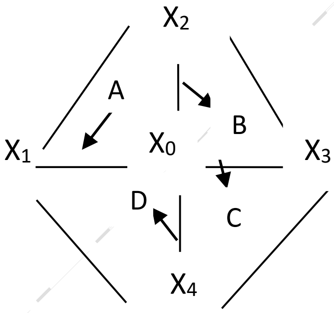

Figure 2: A pyramidal reaction network with four-nodes in the base triangle.

3. Cross-to-square transformation technique was used to transform the cross-network represented by the pathways X_2 to X_4 and X_1 to X_3 to a square network represented by the pathways X_4 to X_1, X_1 to X_2, X_2 to $X_{3,}$ X_3 to X_4. Figure 3 shows the transformed inner cross-network (dash lines). X_0 was considered as an intersection node in the transformation.

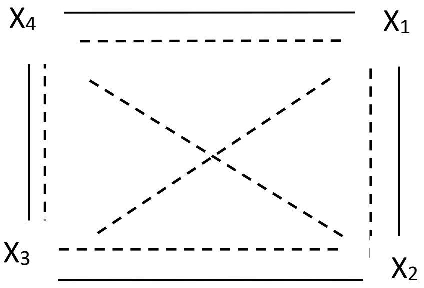

Figure 3: Transformed cross-network into square network.

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4. The parallel pathways between X_3 and X_2, X_2 and X_1, X_1 and X_4, and X_4 and X_3 are lumped into loop coefficients (L_{ij}) where (i,j) stand for (3,2), (2,3), (2,1), (1,2), (1,4), (4,1), (4,3), (3,4).

The system is now reduced to a pyramidal network with three nodes in the base triangle. The network with three nodes in the base triangle is presented in Figure 4.

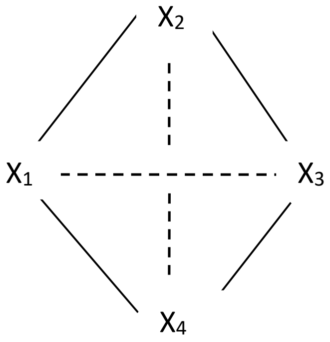

Figure 4: Pyramidal network with three nodes in the base triangle

A cyclic representation of the pyramidal network with three nodes in the base triangle showing inner Y-type network is presented in Figure 5.

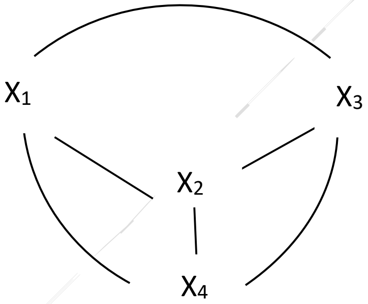

Figure 5: Cyclic representation of pyramidal network

5. Applying Y-to-delta transformation to the Y-network in Figure 5, an equivalent delta-type network is obtained. Transferring the delta-type network into the main cycle, the complete network of the reaction is now reduced to two cycles with two pathways between each node. Figure 6 shows the network containing two cycles and pathways between the three nodes. The dash lines show the delta-type network.

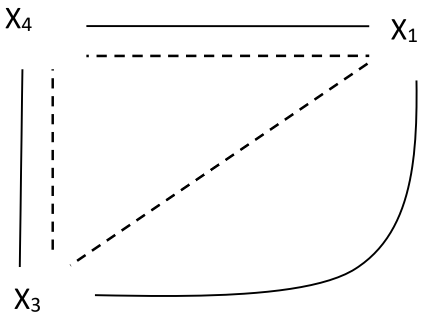

Figure 6: Reduced network containing two cycles and three pathways between nodes.

6. The three parallel pathways between the three nodes in Figure 6 are lumped into loop coefficients to yield a single-cycle reaction network. The single-cycle network is shown in Figure 7.

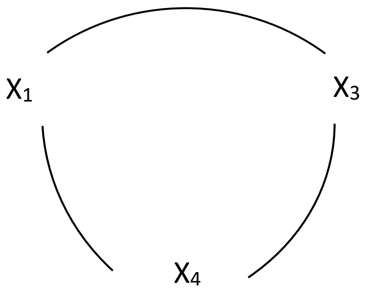

Figure 7: Reduced single cycle reaction network for ethylbenzene isomerization reaction.

The general rate equation for reduced single-cycle developed in Chern and Chen (2003) is then applied to the reduced single-cycle network in figure 6 to get the rate equation through the cycle. Equation 12 shows the general equation for the rate through the cycle.

$$r = \frac{\Delta}{D}[X_T] \qquad 12$$

Where;

$$\Delta = \left(\prod_{i=0}^{n} L_{l,l+1} - \prod_{i=0}^{n} L_{l+1,l} \right)$$, and

$$D = \left\{ \begin{array}{l} D_{ii} + D_{jj} + D_{kk} + \dfrac{\sum\limits_{h=i,j,k} \Lambda_{ho} D_{hh}}{S_0} + \sum\limits_{i}^{k \to i} \left(C_{kl} D_{kk} + C_{il} D_{ii} \right) + \sum\limits_{l}^{i \to j} \left(C_{il} D_{ii} + C_{jl} D_{jj} \right) + \\ \sum\limits_{i}^{j \to k} \left(C_{jl} D_{jj} + C_{kl} D_{kk} \right) + \sum\limits_{p}^{p=i,j,k} \sum\limits_{l}^{path\,p} \left(\dfrac{C^{(p)}{}_{0l}}{S_0} \right) \sum\limits_{h=i,j,k} \Lambda_{ho} D_{hh} + C_{pl}{}^{(p)} D_{PP} \end{array} \right\}$$

The notation Δ in the numerator of equation 12 represents the difference between the product of the forward loop coefficients of the reduced single-cycle network and the product of the reverse rate coefficients. The forward loop coefficients are $L_{13}^{1}, L_{34}^{1}, L_{41}^{1}$ and the reverse loop coefficients are $L_{31,}^{1}\ L_{43}^{1}, L_{14}^{1}$. Hence the notation Δ can be expressed in the form shown in equation 14.

$$\Delta = L_{13}^{1} L_{34}^{1} L_{41}^{1} - L_{31}^{1} L_{43}^{1} L_{14}^{1} \qquad 14$$

The expression for D is evaluated by considering each term in the expression:

1. $D_{ii}, D_{jj}, and\ D_{kk}$ (i, j, and k represent the indices of the node intermediates of the final reduced cycle; that is 1, 3, and 4) are obtained from the loop coefficients of the final reduced

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cycle shown in figure 6. The D_{jk} operator formula shown in equation 4 is used in evaluating the D terms. Equation 15 shows the expression of $D_{ii}, D_{jj}, and\ D_{kk}$

$$\begin{aligned} D_{11} &= L^1_{34}L^1_{41} + L^1_{31}L^1_{14} + L^1_{31}L^1_{43} \\ D_{33} &= L^1_{41}L^1_{13} + L^1_{43}L^1_{31} + L^1_{43}L^1_{14} \\ D_{44} &= L^1_{13}L^1_{34} + L^1_{14}L^1_{43} + L^1_{14}L^1_{31} \end{aligned} \qquad 15$$

2. $\dfrac{\sum\limits_{h=i,j,k} \Lambda_{ho} D_{hh}}{S_0}$

This term denotes the expression for concentration of missed center nodes X_2 used in Y-to-delta transformation. Indices i, j, and k represent indices of the node intermediates of the final reduced cycle; that is 1, 3, and 4. And S_0 is the sum of the segment coefficients (Λ) of the segments from the missed center node intermediate to the adjacent node intermediates (that is; X_1, X_3, and X_4). Consequently, after relevant substitutions, the term is presented in equation 16.

$$\frac{\sum\limits_{h=i,j,k} \Lambda_{ho} D_{hh}}{S_0} = \frac{\Lambda_{10}D_{11} + \Lambda_{30}D_{33} + \Lambda_{40}D_{44}}{\Lambda_{01} + \Lambda_{02} + \Lambda_{03} + \Lambda_{04}} \qquad 16$$

3. $\sum\limits_{l}^{k\to i} \left(C_{kl}D_{kk} + C_{il}D_{ii} \right)$

This term denotes the expression for summation of the concentration of missed intermediates (represented by l) in the pathway k-to-i (k stands for 1 and i stands for 3) due to network reduction. This is expression is 0 (zero) because there are no intermediates in the pathway from X_1 to X_3.

4. $\sum\limits_{l}^{i\to j} \left(C_{il}D_{ii} + C_{jl}D_{jj} \right)$

This term denotes the expression for summation of the concentration of missed intermediates (represented by l) in the pathway i-to-j (i stands for 3 and j stands for 4) due to network reduction. This is expression is 0 (zero) because there are no intermediates in the pathway from X_3 to X_4.

5. $\sum\limits_{l}^{j\to k} \left(C_{jl}D_{jj} + C_{kl}D_{kk} \right)$.

This term denotes the expression for summation of the concentration of missed intermediates (represented by l) in the pathway j-to-k (j stands for 4 and k stands for 1) due to network reduction. This is expression is also 0 (zero) because there are no intermediates in the pathway from X_4 to X_1.

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6. $$\sum_{p}^{p=i,j,k} \sum_{l}^{path\, p} \left(\frac{C^{(p)}{}_{0l}}{S_0} \right) \sum_{h=i,j,k} \Lambda_{ho} D_{hh} + C_{pl}{}^{(p)} D_{PP}$$

This generally represents the concentration of missed intermediates as a result of network reduction between center-node and i, center-node and j, and center node and k (i, j, and k represent the indices of the nodes that make the final reduced cycle; that is 1, 3, and 4). This expression is also 0 (zero) because there are no intermediates between the nodes that make up the final reduced cycle and the centre-node.

Following relevant substitutions, the D term is presented in equation 17.

$$D = \begin{pmatrix} \left(L_{34}^{1} L_{41}^{1} + L_{31}^{1} L_{14}^{1} + L_{31}^{1} L_{43}^{1} \right) + \\ \left(L_{41}^{1} L_{13}^{1} + L_{43}^{1} L_{31}^{1} + L_{43}^{1} L_{14}^{1} \right) + \left(L_{13}^{1} L_{34}^{1} + L_{14}^{1} L_{43}^{1} + L_{14}^{1} L_{31}^{1} \right) \end{pmatrix} + \left(\frac{\Lambda_{10} D_{11} + \Lambda_{30} D_{33} + \Lambda_{40} D_{44}}{\Lambda_{01} + \Lambda_{02} + \Lambda_{03} + \Lambda_{04}} \right) \quad 17$$

Substituting equations 14 and 17 into equation 12, the expression for the rate through the reduced single cycle is obtained.

$$r = \frac{L_{13}^{1} L_{34}^{1} L_{41}^{1} - L_{31}^{1} L_{43}^{1} L_{14}^{1}}{\begin{pmatrix} \left(L_{34}^{1} L_{41}^{1} + L_{31}^{1} L_{14}^{1} + L_{31}^{1} L_{43}^{1} \right) + \\ \left(L_{41}^{1} L_{13}^{1} + L_{43}^{1} L_{31}^{1} + L_{43}^{1} L_{14}^{1} \right) + \left(L_{13}^{1} L_{34}^{1} + L_{14}^{1} L_{43}^{1} + L_{14}^{1} L_{31}^{1} \right) \end{pmatrix} + \left(\frac{\Lambda_{10} D_{11} + \Lambda_{30} D_{33} + \Lambda_{40} D_{44}}{\Lambda_{01} + \Lambda_{02} + \Lambda_{03} + \Lambda_{04}} \right)} [X_T] \quad 18$$

Equation 18 shows the rate equation through the reduced single cycle network presented in figure 6.

2.2 Parameter Estimation

A well-known task in the concise mathematical representation of reaction network and mechanism is the estimation of the reaction rate constants. Parameter estimation is essentially an optimization problem whereby the unknown parameters are obtained by minimizing a suitable objective function (Englezos and Kalogerakis, 2001). The objective function represents a measure of disparity between observed reaction rates from experimental data to rate from developed model. The Nelder- Mead simplex optimization technique was used in this study to minimize the objective function. The Nelder-Mead simplex algorithm is a direct search method for multidimensional unconstrained minimization. The algorithm seeks to minimize a scalar valued nonlinear function of n real variables using only scalar function values without any derivative.

The optimization routine was carried out using MATLAB computer software. The MATLAB solver that executes optimization routine based on Nelder-Mead technique is the nonlinear programming solver *fminsearch*. The solver uses the Nelder-Mead optimization algorithm as elucidated by Lagarias *et al* (1998).

3. Results and Discussion

The model developed is presented in equation 18. Table 1 shows the rate constants for each reaction step. The calculated values of activation energy and frequency factor for the model is presented in Table 2.

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Table 1: Estimated Rate Constants

Rate constants (mol h^{-1} g_{cat}^{-1})	T = 593 K	T = 613 K	T = 633K	T = 673 K
K_{01}	5.1845	-10.2268	10.404	1.4783
K_{02}	2.4713	-964	-1.4413	-0.3023
K_{03}	13.7876	-15.6994	4.129	-0.2102
K_{04}	5.3871	0.9333	-12.9715	-0.5389
K_{10}	-26.2378	-55.2825	-31.5937	-0.8001
K_{20}	-1.6024	-2.9293	1.2157	2.7953
K_{30}	6.3507	6.5799	6.7756	2.1114
K_{40}	3.646	16.5405	15.957	1.4358
K_{12}	-10.3324	12.9313	-14.6375	1.3043
K_{21}	3.3084	6.7447	23.2739	1.3722
K_{23}	-0.2239	-7.7967	7.8819	0.5419
K_{32}	2.7019	0.1671	0.7595	1.906
K_{34}	7.7078	-4.0816	0.4403	-1.1509
K_{43}	6.9018	4.6199	12.9419	0.0532
K_{14}	5.9099	13.9132	12.0624	5.4539

The model developed in this study clearly depicts the multi-step nature of the reaction. The embedded partial pressure terms in the denominator of the rate expression indicate the adsorption of the reacting species on the surface of the catalyst as the reaction mechanism suggests (Fogler, 2004). The loop coefficients in the models expressively show that the reaction consist of several pathways as represented by the reaction network. The model also shows the contribution of each elementary step in the reaction network to the kinetics of the overall reaction. This is as indicated by the appearance of the rate constants of each step in the model developed. The L^{1}_{ij} terms appearing in the model equations constitute the rate constants of the all steps. As it is customary to observe the effect of temperature variation on the estimated rate constants, a general pattern is not observable in the results obtained. Some of the values obtained for the rate constants deviate from expected trend. Comparing the values for the constants with that reported by Farahani *et al* (2020) further indicates a departure although with a justification. In their work, the rate constants for the reaction step producing m-xylene at temperatures of 653K, 663K, and 673K were reported to be 48.74 mol h^{-1} g_{cat}^{-1}, 58.47 mol h^{-1} g_{cat}^{-1}, and 72.29 mol h^{-1} g_{cat}^{-1} respectively. That of the reaction step producing p-xylene at the same temperatures were reported to be 9.72E 06 mol h^{-1} g_{cat}^{-1}, 1.11E 06 mol h^{-1} g_{cat}^{-1}, and 1.28E 06 mol h^{-1} g_{cat}^{-1} respectively. The rate constants for the reaction step producing m-xylene in this study are 7.7078 mol h^{-1} g_{cat}^{-1} and 0.4403 mol h^{-1} g_{cat}^{-1} at 593K and 633K. While the rate constants for the reaction step producing p-xylene at the same temperatures are 7.8819 mol h^{-1} g_{cat}^{-1} and 0.5419 mol h^{-1} g_{cat}^{-1} respectively. A significant discrepancy can be observed in the reported values when compared. This can be attributed to the different modelling techniques adopted in the two works, slight difference in the starting material, and the choice of catalyst. It is already established that the nature of catalyst used for the reaction of interest affects the reaction rate constants (Farahani, 2020). An anomaly was also observed in the values of pre-exponential factor calculated. The values as shown in table 2 appear to be constant all through. This did not compare favorably well

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with expected trend although literature values are scanty as much work is not reported on the methodology adopted in this study. The expected anomaly in the value of activation energy for multi-step reactions is confirmed in the results presented in table 2. This is evident in some negative values of the activation energy calculated.

Table 2: Calculated Arrhenius Parameters in the Model

Rate Constants	Activation Energy (kJ/mol)	Frequency Factor
K_{01}	2.49E-05	2.722635
K_{02}	8.31E-04	2.722635
K_{03}	2.49E-04	2.722635
K_{04}	4.16E-04	2.722635
K_{10}	0.00E+00	2.722635
K_{20}	6.65E-04	2.722635
K_{30}	4.16E-04	2.722635
K_{40}	2.49E-05	2.722635
K_{12}	4.16E-05	2.722635
K_{21}	-4.16E-05	2.722635
K_{23}	-8.31E-05	2.722635
K_{32}	4.16E-05	2.722635
K_{34}	3.32E-04	2.722635
K_{43}	8.31E-05	2.722635
K_{14}	-8.31E-05	2.722635
K_{41}	-5.82E-04	2.722635

For multi-step reactions, the activation energy may be negative and the rate decreases with increasing temperature (Helfferich, 2004). This indicates that the rates of reverse steps in the reaction network increases more sharply with temperature than those of forward steps for cases in which the activation energy is negative.

4. Conclusions

The Bodenstein approximation of trace-level intermediates was exploited in this study to effectively model ethylbenzene isomerization reaction over Pt/Al_2O_3. Reasonable assumptions were considered in the model development alongside network transformation techniques that helped reduce the complex reaction network with multi pathways and intersection into a single cycle network. Few deviations were seen in the results presented in the study even though the model development procedure compares well with the available literature. Discrepancies were seen in the rate constant values reported in an earlier study but the non-alignment can be

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attributed to the choice of modeling technique and catalyst used. Findings from the study re-echo the reliability of fundamental approach in up-scale applications; this is evident in the consideration of the individual molecular steps of the reaction in the model development. General rate equation approach to kinetic study is recommended for elucidating the kinetics of complex reactions and Bodenstein approximation alongside network transformation techniques are also recommended for effective modeling of multi-step reactions without loss in vital information.

Nomenclature

EB, A	Ethylbenzene
OX, B	*o*-xylene
PX, C	*p*-xylene
MX, D	*m*-xylene
EBS, X_1	Ethylbenzene complex
OXS, X_2	*o*-xylene complex
PXS, X_3	*p*-xylene complex
MXS, X_4	*m*-xylene complex
S, X_0	free catalyst site
i, j	indices indicating reaction step
λ_{ij}	Pseudo-first order rate coefficient
D	Denominator of segment coefficient equation
Λ	Segment coefficient
X_j	intermediate at j^th^ position
X_i	intermediate at i^th^ position
$r_{j \to k}$	Rate of reaction from j-to-k
X_T	Total catalyst concentration

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