

CONVERSION OF NORMAL HEXANE AND METHYLCYCLOPENTANE INTO BENZENE BY USING REFORMING CATALYST *

by

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ABSTRACT

As the significant amount of paraffins and naphthenes in the reforming feedstock, the conversion of these hydrocarbons to aromatic in the catalytic reforming process thus plays an important role. An experiment has been carried out to study the reaction rate of normal hexane and methylcyclopentane into benzene by using reforming catalyst.

I. INTRODUCTION

The rapidly increasing demand for aromatic hydrocarbon as petrochemical feedstock has promoted refiners to seek methods of improving yields of these valuable products.

Catalytic reforming of naphtha is one of the aromatic production from petroleum (1). As paraffins and naphthenes are usually the major component of the naphtha feedstock (2), high conversion of these paraffins and naphthenes to aromatic plays an important role.

In order to obtain a better understanding about the aromatization of normal hexane and C₅-ring naphthenes, an experiment has been carried out to study the reaction rate of normal hexane and methyl cyclopentane into benzene, with the operating conditions : temperature: from 450^o to 490^oC, pressures : from 10 to 30 kg/cm² and H₂/HC ratio : from 4 to 12 mole/mole, using reforming catalyst.

A Catatest unit operated in a continuous system was used in these experiments. Gas and liquid product samples taken from gas and liquid samplers respectively were analysed by using gas liquid chromatography.

II. EXPERIMENTAL

Pure grade of normal hexane and methylcyclopentane were used as feedstocks.

The purified hydrogen, with impurity less than 0,5% by vol and bi-metallic reformer catalyst were used in this experiment.

Experiment was carried out in a micro-catatest unit, without gas recycle, operated at high temperature and pressure with a continuous system. The volume and inside diameter of the reactor are 200 cc and 19 mm respectively. The reactor temperature is regulated automatically.

Gas and liquid product samples were taken from gas and liquid sampler respectively and analysed by using Gas-Liquid Chromatography.

III. RESULTS AND DISCUSSIONS

A. Reaction Rate

Activation energy of conversion of n-hexane and methylcyclopentane is calculated by using the following Arrhenius equation :

$$k_1 = A_1 e^{-E/RT}$$

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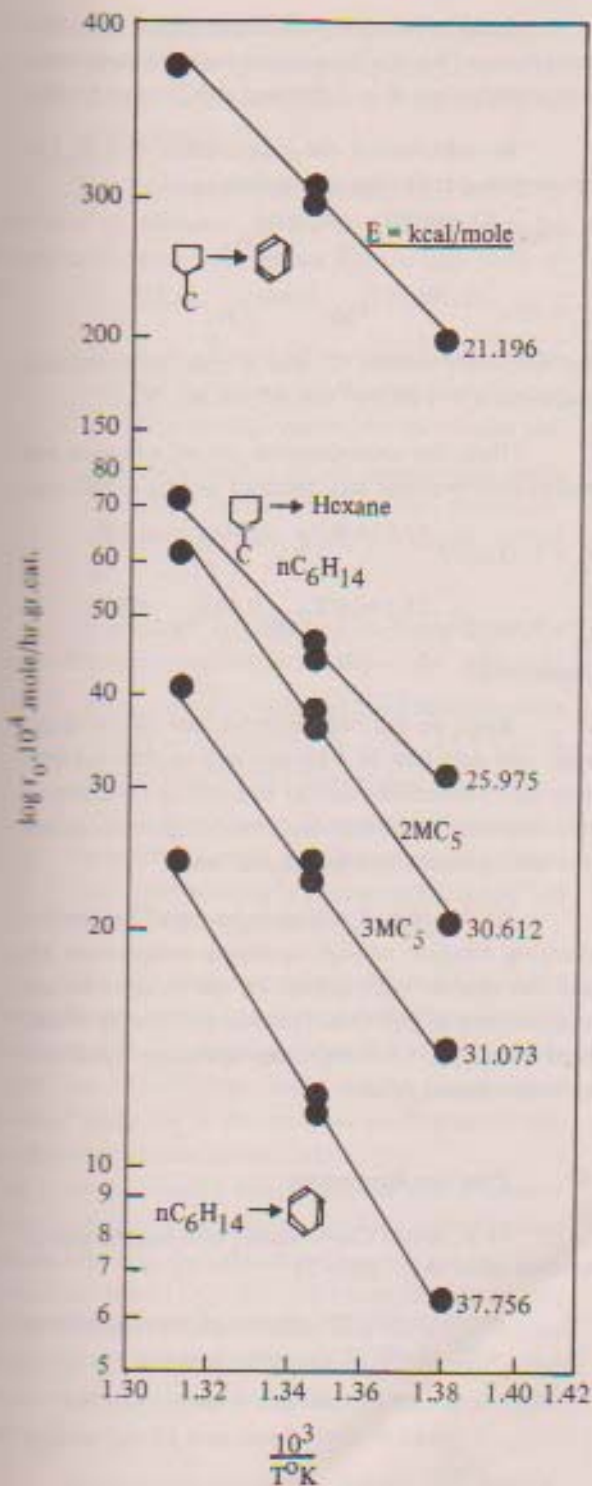


Figure 1 : A plot of $\log r_0$ againsts $10^3/T^0K$

The initial rate (r_0) is proportional to the rate constant (k_1). Figure 1 shows a plot of $\log r_0$ against $1/T^0K$, where its slope is equal to $-E/2.303 R$. And the activation energy of conversion of n-hexane and methylcyclopentane to benzene, 3 methylpentane, 2 methylpentane and n-hexane are 37.756, 21.196, 31.073, 30.612 and 25.975 kcal/mole respectively.

The rate of n-hexane and methylcyclopentane conversion can be written as follow, (3) :

$$r_0 = k_2 P_{HC}^{\alpha} P_{H_2}^{\beta}$$

If H_2/HC ratio is kept constant, the rate becomes :

$$r_0 = k_3 P_T^{(\alpha + \beta)}$$

or $\log r_0 = (\alpha + \beta) \log P_T + \log k_3$

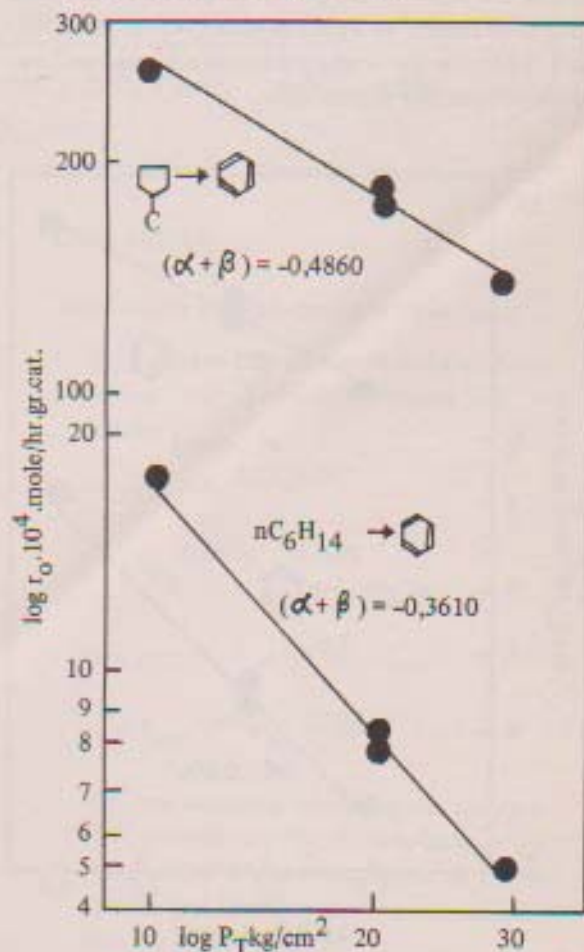


Figure 2 : A plot of $\log r_0$ againsts $\log P_T$

Figure 2 shows a plot of $\log r_o$ against $\log P_T$ for n-hexane and methylcyclopentane aromatization. The slope is equal to the total orders of the reaction rate ($\alpha + \beta$), and is found to be $(\alpha + \beta) = -0,361$ and $-0,486$ for aromatization of n-hexane and methylcyclopentane respectively.

If the P_{H_2} is kept constant, the above rate equation becomes :

$$r_o = k_4 P_{HC}^\alpha ; \text{ or}$$

$$\log r_o = \alpha \log P_{HC} + \log k_4$$

Figure 3 shows a plot of $\log r_o$ against $\log P_{HC}$ for n-hexane and methylcyclopentane aromatization. The slopes are equal to the partial orders of the reaction rate with respect to hydrocarbons (α) i.e. $\alpha = 0,969$ and $0,441$ for the aromatization of n-hexane and methylcyclopentane respectively.

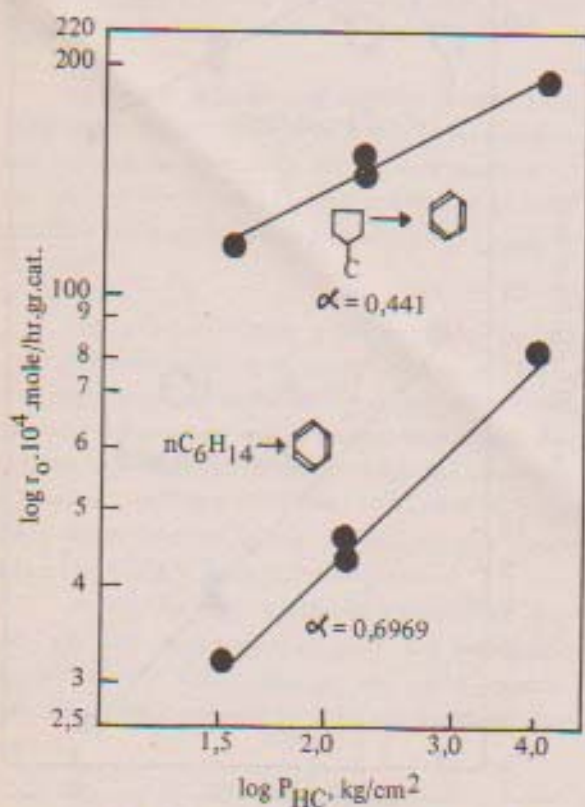


Figure 3 : A plot of $\log r_o$ against $\log P_{HC}$

And the reaction order with respect to hydrogen pressure (β) of n-hexane and methylcyclopentane aromatization are $\beta = -1,330$ and $-0,927$ respectively.

By substitution the experimental rate (r_o) to the empirical following rate equations :

$$r_o' = A' \cdot e^{-37,754/RT} P_{C_6}^{0,969} P_{H_2}^{-1,330}$$

$$r_o'' = A'' \cdot e^{-21,196/RT} P_{MC}^{0,441} P_{H_2}^{-0,927}$$

the frequency factors A' and A'' can be calculated, and leads $A' = 1,68 \cdot 10^8$ and $A'' = 3,65 \cdot 10^5$.

Then the aromatization rate of n-hexane and methylcyclopentane into benzene will be as follows :

$$r_o' = 1,63 \cdot 10^8 e^{-37,754/RT} P_{C_6}^{0,969} P_{H_2}^{-0,330}$$

$$r_o'' = 3,67 \cdot 10^5 e^{-21,196/RT} P_{MC}^{0,441} P_{H_2}^{-0,927}$$

respectively.

Based on the experimental data of the empirical rate equation of n-hexane and methylcyclopentane into benzene shows that rate will be favorable on the following operating conditions : high temperature, low total pressure and low H_2/HC ratio.

As the rate of n-hexane (or paraffins) hydrocracking increase at high operating temperature (4) and the rate of coke deposit on the catalyst surface will increase at low total pressure and low hydrocarbons ratio (5), so those three operating conditions have on optimal value.

B. Reaction Mechanism

By products (iso-hexanes) of n-hexane aromatization show that (Table 1).

- By increasing the operating temperature from 450° to $490^{\circ}C$ the ratios between :
 - . 2 methyl pentane and 3 methyl pentane
 - . 2 (two) methyl chains and 1(one) methyl chain.

increase from 1,29 to 1,44 mole/mole and from 0,054 to 0,092 mole/mole respectively.

But these ratios are nearly constant by increasing the operating pressures (from 10 to 30 kg/cm²) and H₂/HC ratio (from 4 to 12 mole/mole).

The increasing of iso-hexanes obtained as by products of n-hexane dehydrocyclization with the operating temperature suggests that the high yield of:

- The isomerization of the intermediate molecule of the primer carbonium ion (n-hexyl ion) into the high isomerized carbonium ion.
- The decyclization of the intermediate molecule of the cyclic carbonium ion (methylcycloamyl ion) into 2 methyl and 3 methyl amyl ions.

By products (normal and iso-hexanes) of methylcyclopentane aromatization show that : (Table 1)

- n-hexane has a high yield and low activation energy of formation, i.e. 39.4 : 44.4 mole % on the total hexane products.
- The ratio between 2 methylpentane and 3 methylpentane is nearly constant by increasing the operating temperature from 450^o to 490^oC i.e. \pm 1,60 mole/mole.

The high yield by product of n-hexane and the low activation energy of n-hexane formation from the aromatization of methylcyclopentane it suggest that primer ion of methylcycloamyl will be a major intermediate molecule in the reaction mechanism of this methylcyclopentane aromatization. (7)

The ratios between 2 methylpentane and 3 methylpentane obtained as by products of the aromatization of n-hexane and methylcyclopentane into benzene are almost the same : i.e. 1.29 : 1.44 mole/mole and 1.58 : 1.60 mole/mole. Thus it seems that the methylcycloamyl ion will be a major intermediate molecule in the reaction mechanism of n-hexane conversion into benzene. (8)

By products ratios of n-hexane and methylcyclopentane (x) conversion with various operating conditions (mole/mole).

Table 1

Temperature (°C)	450 ^o	470 ^o	490 ^o C
22DMC ₄ /2MC ₅ + 3MC ₅	0.054	0.070	0.092
2MC ₅ /3MC ₅	1.29	1.36	1.44
2MC ₆ /2MC ₆ + 3MC ₅ ^(x)	0.79	0.71	0.67
2MC ₅ /3MC ₅ ^(x)	1.6	1.58	1.60
Total Pressures (kg/cm ²)	10	20	30
22DMC ₄ /2MC ₅ + 3MC ₅	0.055	0.054	0.051
2MC ₅ /3MC ₅	1.33	1.31	1.28
H ₂ /HC ratio (mole/mole)	4	8	12
22DMC ₄ /2MC ₅ + 3MC ₅	0.054	0.056	0.059
2MC ₅ /3MC ₅	1.29	1.31	1.31

IV. CONCLUSION

Based on the experimental data show that :

1. The reaction rate of the aromatization of hexane and methylcyclopentane are as follows :

$$r_0' = 1.63 \cdot 10^8 e^{-37,754/RT} \times P_{C_6}^{0,969} P_{H_2}^{-1,330}$$

$$r_0'' = 3.67 \cdot 10^5 e^{-21,196/RT} \times P_{MC}^{0,441} P_{H_2}^{-0,927}$$

2. The tree operating conditions i.e. temperature, pressure and H₂/HC ratio have an optimum value for the conversion of the n-hexane and methylcyclohexane into benzene for a given catalyst.
3. It suggests that the methylcycloamyl ion

will be a major intermediate molecule in the reaction mechanism of the n-hexane aromatization.

V. NOTATION

A, A', and A'' = are the frequency factors.
 C_6 = is normal hexane.
 E = is activation energy-kcal/mole.
 H_2 , HC and H_2/HC = are hydrogen, hydrocarbons and the mole ratio between H_2 and HC respectively.

k_1, k_2, k_3, k_4 = are the rate constants.
 MC = is methylcyclopentane.
 P_{HC}, P_{H_2}, P_{C_6} = are the partial pressure of hydrocarbons, hydrogen, n-hexane, methylcyclopentane and the total pressure respectively.
 P_{MC} and P_T
 R = is the gaseous constants.
 r_0, r_0', r_0'' = are the reaction rates.
 α and β = are the partial order reaction with respect to hydrocarbons and hydrogen respectively.

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