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Kinetic Study of Catalytic Hexane Isomerization

Abdul Halim A.K. Mohammed[*],Ameel M. Rahman and Maha Al-Hassani[*]

[*]*Chemical Engineering Department - College of Engineering - University of Baghdad – Iraq*

Abstract

The isomerization of n-hexane on platinum loaded acidic zeolite was studied at atmospheric pressure, H2/nC6 molar ratios of 1-4 and temperature range of 240-270ºC.
The measured kinetic data were fitted to an equation based on the bifunctional mechanism and by using independently obtained dehydrogenation and adsorption data. The activation energies of protonation (ΔHpro) and the elementary isomerization step (Eact,iso) and as well as the corresponding preexponential factor were simultaneously determined. The observed values of both ΔHpro and Eact,iso are in agreement with the results of quantum-chemical calculations.

Introduction

More stringent limits on the amount of aromatics that may be included in gasoline have resulted in a renewed interest in the skeletal isomerization of n-alkanes with a view to use the branched isomers as octane-enhancing components. Branched isomers are more desirable because of their higher octane number. At equilibrium lower temperatures favor branched isomers; therefore there has been an effort to develop catalysts that are effective at 270ºC or less. Over the past several decades the progression has been from Pt/Al2O3, which is active for n-hexane isomerization in the 450-500ºC range to Pt/chlorinated Al2O3, which is active in the 350-400ºC range and more recently to Pt/H-zeolite catalysts, which are active in the 200-270ºC range. Additional research has been carried on Pt/sulfated ZrO2, Pt/WOx-ZrO2 and related materials (1).

Based on the earlier studies of Mills et al. (2) a bifunctional mechanism for isomerization as follows; (i) dehydrogenation of alkane occurs at the metal centre (ii) the resulting alkene molecule is isomerized at an acid site and (iii) the isomerized alkene intermediate is hydrogenated at the metal centre to form the product (3). Molecular hydrogen is added to

The system in order to enhance isomerization selectivity and prevent deactivation of the catalyst.

The bifunctional mechanism is somewhat misleading since it suggests that protonation of the alkene generates carbenium ions in the same way as occur in liquid-phase super acids (4). However, quantum chemical calculations have shown that protonation of alkenes on solid acid sites renders so-called alkoxy species as stable reaction intermediates which are bonded to the lattice by strong covalent C-O bond(s). These calculations suggest that carbenium ion like species only exist as a transition state at the (de) protonation reaction. Due to the formation of strong covalent bonds, the enthalpy of protonation (ΔHpro) is expected to be high; the same holds for the activation energy of the isomsrization step (Eact,iso). To calculate Eact,iso from kinetic measurements, Eact,iso is expressed as a function of a number of parameters (5) including the apparent energy and, which is the actually measured quantity, and ΔHpro, for which nearly only quantum-chemical calculations are available. Therefore values for Eact,iso determined in this way may also be unreliable.

In conclusion, a meaningful kinetic analysis should involve an experimental determination of ΔHpro.

In the present study, the kinetic data are analyzed using a rate equation based on the bifunctional mechanism, which allows for the determination of Eact,iso and ΔHpro. To distinguish between the effects of adsorption and the intrinsic kinetics on the reaction rate, independent adsorption data are used.

Kinetic Analysis

If it is assumed that the isomerization step is the rate determining and conversion is so low then the reverse reaction can be neglected. It can be assumed that the dehydrogenation steps are equilibrated as reported by Maha Al-Hassani (6)

The dehydrogenation enthalpy (ΔHdh) and preexponential factor of K_{dh} (K_{dh}^o), were calculated from standard enthalpy and entropy of formation of n-hexane and of all branched hexane isomers;

$$\Delta Hdh \approx \Delta Hof\ hexane - \Delta Hof\ hexane \qquad (1)$$

$$K^o{}_{dh} = P^\theta e^{\frac{\Delta S^o_{f\ hexene} - \Delta S^o_{f\ hexane}}{R}} \qquad (2)$$

Where, $\Delta H^o_{f,i}$ and $\Delta S^o_{f,i}$ are respectively the standard enthalpy and entropy of formation of component (i) in the gas phase (the temperature dependence of $\Delta H^o_{f,i}$ and $\Delta S^o_{f,i}$ was neglected) and P^θ is the standard pressure (P^θ =101,325 Pa). The value of $\Delta S^o_{f,i}$ and $\Delta H^o_{f,i}$ of n-hexane and n-hexene were taken from the work of reference (7). Although k_{dh} refers to adsorbed phase, it is assumed that the difference between the formation enthalpy/entropy in the gas phase and the adsorbed phase is equal for n-hexane and n-hexene, so that the enthalpy/entropy of dehydrogenation is equal in both phase (the calculation in eqns. [1] and [2] can be safely made, since the values for individual isomers vary by less than 10%).

The adsorption parameters for zeolite were taken from studies published by Eder and Lercher (8, 9). The preexponential factors in units (Pa-1) were calculated from Henery's constant KH (in units mmol/g.atm) measured at temperature Tm using equation [3].

$$K_{ads}(T_x) = \frac{K_H(T_m)}{P^o Q_{max} \exp\left(-\dfrac{\Delta H_{ads}}{RT_m}\right)} \qquad \dots (3)$$

Where Q_{max} denote the maximum concentration of n-hexane in the porous crystals (in unit's mol/kg). The value of Q_{max} was extracted from literature (8, 10).

The net number of isomerized molecules produced per unit time per acid site is called the turnover frequency (TOF) and is given by Maha Al-Hassani (6):

$$TOF = \frac{k_{iso}^b K_{ads} K_{pro} K_{dh} \dfrac{P_n}{P_{H_2}}}{K_{ad}P_n + K_{ad}K_{dh}\dfrac{P_n}{P_{H_2}} + K_{ad}K_{pro}K_{dh}\dfrac{P_n}{P_{H_2}} + 1} \qquad (4)$$

Where, K_{ads}, K_{dh} and K_{pro} are the equilibrium constants of, respectively adsorption, dehydrogenation, and protonation for n-hexane; K_{iso} is the rate constant of conversion of the intermediate n-hexyl alkoxide into iso-hexyl alkoxide (no distinction is made between the various isomers) P_{H2} is the hydrogen pressure; and P_n is the n-hexane pressure. Equation (4) can be linearized by taking the reciprocal expression:

$$\frac{1}{TOF} = \frac{P_{H_2}}{k_{iso}^b K_{pro} K_{dh}} + \frac{1}{k_{iso}K_{pro}} + \frac{1}{k_{iso}^b} + \frac{P_{H_2}}{k_{iso}^b K_{ads} K_{pro} P_n} \qquad (5)$$

The plot of 1/TOF vs. 1/p_n should be linear, and since K_{ads} and K_{dh} are known or can be determined from independent experiments, K_{iso} and K_{pro} can be calculated from the slope(s) and intercept (i):

$$k_{iso} = \frac{P_{H_2}}{iP_{H_2} - s\ K_{ads}P_{H_2} - s\ K_{ads}K_{dh}} \qquad (6)$$

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$$K_{pro} = \frac{i}{s}\frac{P_{H_2}}{K_{ads}K_{dh}} - \frac{P_{H_2}}{K_{dh}} - 1 \qquad (7)$$

By determining K_{iso} and K_{pro} as a function of temperature and plotting ln K_{iso} and ln K_{pro} vs. the reciprocal temperature, respectively, Eact, iso and ΔH_{pro} can be obtained.

Experimental and Materials

n-Hexane supplied by BDH with 99% purity was used as a feedstock for isomerization experiments. HY-zeolite (CBV 600) catalyst powder was supplied from Zeolyst International and used as a support for catalyst preparation. 100 g of HY zeolite powder was mixed with 30% montmorillonite clay as binder as suggested by Murry (11). The resulting mixture was mixed with water to form a paste. An extrudates with 0.3 cm were formulated and dried over night at 100°C, then 0.3 wt%Pt/HY-zeolite was prepared by impregnation method with a proper solution of hexachloroplatinic acid. The impregnated extrudates were dried at 110°C then calcinated at 300°C for 3 hours in furnaces with dry air (12). The calcinated catalyst was then reduced with hydrogen at 350°C for 3 hours (13).

Procedure and Equipments

The catalytic unit performance tests were carried out in a continuous fixed bed reaction unit. The reactor was a carbon steel tube with an outside diameter of 1.9 cm, 2 mm thick and 80 cm length. 0.3wt%Pt/HY-zeolite catalyst was charged between two layers of inert materials (glass balls). The catalytic reactions were carried out in the temperature range of 240-270°C, LHSV of 1-4 h-1, H2/nC6 mole ratio of 1-3 and atmospheric pressure.

n-Hexane partial pressure was kept at 0.28 bar while hydrogen pressure varied between 0.29-0.56 bar using nitrogen as a makeup gas. The nitrogen pressure varied between 0.16-0.45 bar to obtain the final atmospheric reaction pressure.

Liquid products were trapped by condenser at -5°C, collected periodically and analyzed by using gas chromatography. The gas chromatography model 438Aa-VSA supplied by Agilent technologies company was used for the analysis. This device equipped with column of 0.25mm diameter 100m length and FID detector.

Results and Discussion

The adsorption parameters were calculated using the available thermodynamics data (9-14) using equation [3]. These results are tabulated in Table (1).

Table 1, Adsorption parameters.

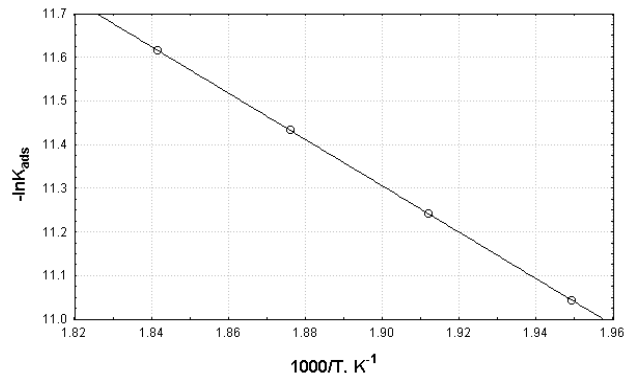| T_x(K)	$K_{ads(Tx)}$(Pa^{-1})
513	1.60×10^{-5}
523	1.31×10^{-5}
533	1.08×10^{-5}
543	9.08×10^{-6}

Fig.1: Shows The Plot of $\ln K_{ads}$ vs. Reciprocal Temperature for ΔH_{ads} Calculation

ΔH_{ads} of 44.2 kJ/mol was obtained from Figure 2. Since the heat of adsorption is exothermic, the adsorption-equilibrium constant K_{ads} decreases with increasing temperature. The preexponential factor of adsorption equilibrium has a value of 5.08×10-10Pa-1

The dehydrogenation parameters were presented in Table (2) using equation [1] and equation [2]. Which ΔH_{dh} equals to 118kJ/mol (4). Since the dehydrogenation is endothermic process, the dehydrogenation-equilibrium constant K_{dh} increases with increasing temperature. The preexponential factor of dehydrogenation reaction has a values of 3.868×1010 Pa. This values are agreed well with the reported results (4, 15, 16).

Table 2, Dehydrogenation parameters.

TX (K)	Kdh(Tx)(Pa)
513	0.3733
523	0.63
533	1.05
543	1.72

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Catalyst Activity

The conversion rates of n-hexane were calculated from the slops of conversion isotherms represents as a function of space time which expressed by gram catalyst per moles of n-hexane feed per second, (g_{cat}s/mol). Apparent activation energies were determined from temperature dependence of the rates of the total conversion, according to the Arrhenius equation (17).

According to the differential method the derivative $\dfrac{dx_{nC_6}}{wF_{nC_6}}$ evaluated from experimental data was used to obtain the reaction rate r_{nC_6} .

The obtained overall rate of reaction is normalized to the number of acid sites. The values of the r_{nC_6} were used for TOF calculations is generally proportional to the catalyst concentration and surface area of the catalyst, so a turnover frequency (TOF) as number of moles reactant converted per mole of Brönsted acid sites per unit time must be calculated.

Figure 2 is used for the simultaneous determination of K_{iso} and K_{pro} from slopes and intercepts of 1/TOF vs. $1/P_{nc6}$ lines plots according to equation (5). Table (3) shows the values of K_{iso} and K_{pro} estimated at P_{H2}=0.57bar and P_{nc6} ranging from 0.14-0.42bar.
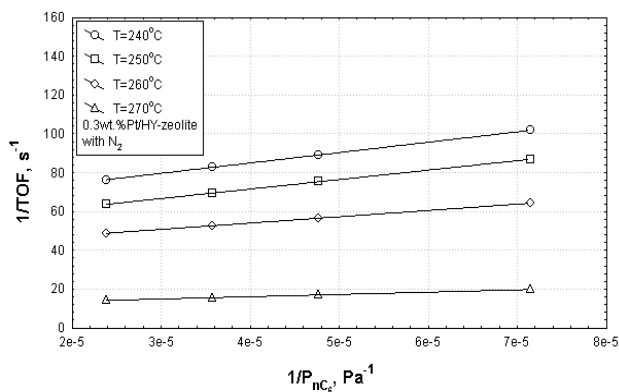

Fig.2 Experimental reciprocal rate equation plots obtained for n-hexane isomerization.

Table 3 Isomerization and Protonation Parameters.

T_X (k)	K_{iso} (sec^{-1})	K_{pro} (-)
513	1.82 x10^{-2}	9.84 x10^{+5}
523	2.19 x10^{-2}	6.41 x10^{+5}
533	2.67 x10^{-2}	5.75 x10^{+5}
543	9.67 x10^{-2}	3.24 x10^{+5}

A high value of K_{pro} indicates that the olefin protonation equilibrium entirely displaced toward the formation of carbenium ion as reported by Riberiro and Gauw et al. (4).

The measured protonation energy -74kJ/mol from Fig.3 is agree well with those obtained by of quantum-chemical method of Kazansky et al. (19) and Viruela et al. (20).
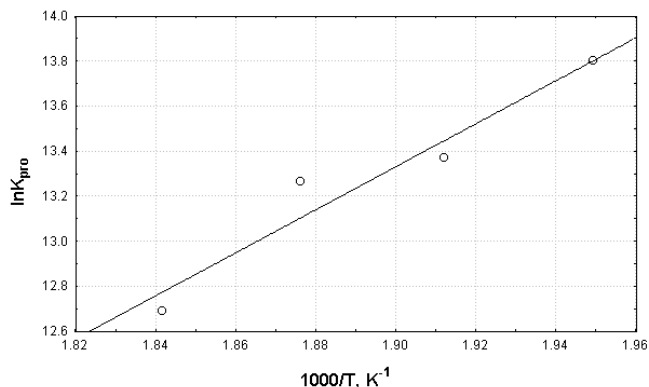

Fig.3, Plot of lnK_{pro} vs. Reciprocal Temperature.

The value of $E_{act,iso}$ was 119.7kJ/mol obtained from Fig.4. The preexponential factor of protonation and isomerization reaction have a value 125.2 and 2.2×10^{11}, respectively and within the experimental temperature range of 240-270ºC, the variation in the rate coefficient of branching rearrangement was relatively small, leading to the conclusion that observed differences in turnover frequencies for the various catalysts was predominantly caused by differences in the adsorption constants.
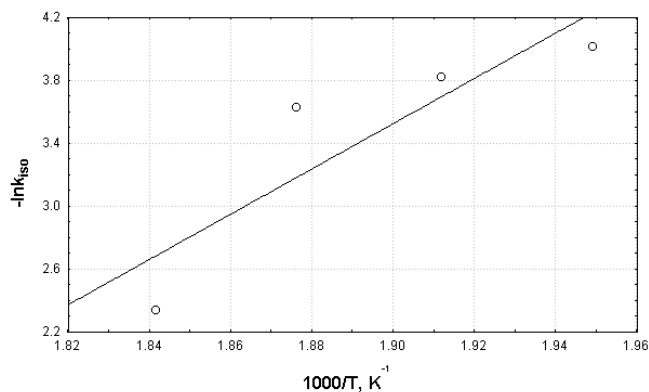

Fig.4 Plot of lnk_{iso} vs. Reciprocal Temperature.

It was possible to simultaneously determined the energy of protonation and energy of branching rearrangement as well as correspondingly preexponentioal factor by fitting the measured kinetic data to an equation based on the bifunctional mechanism and using independency the obtained dehydrogenation and adsorption data as follows:

$$k_{iso} = 2.2 \times 10^{11} \exp\left(-119.7 \times 10^3 / RT\right) \qquad \dots (5)$$

$$K_{ads} = 5.08 \times 10^{-10} \exp\left(+44.2 \times 10^3 / RT\right) \quad \dots (6)$$

$$K_{dh} = 3.86 \times 10^{10} \exp\left(-118.0 \times 10^3 / RT\right) \qquad \dots (7)$$

$$K_{pr} = 125.2 \exp\left(+79 \times 10^3 / RT\right) \qquad \dots (8)$$

Consider these terms in equation (4), the overall rate equation per acid sites was obtained by equation 9:

$$TOF = \frac{5.4 \times 10^{14} \exp\left(-114.5 \times 10^3 / RT\right)\left(P_{nC6} / P_{H2}\right)}{\left(\begin{array}{c} 1 + 510^{-10} \exp\left(44.2 \times 10^3 / RT\right)P_{nC6} \\ + 19.6 \exp\left(-73.8 \times 10^3 / RT\right)\left(P_{nC6} / P_{H2}\right) \\ + 2.5 \times 10^3 \exp\left(-5 \times 10^3 / RT\right)\left(P_{nC6} / P_{H2}\right) \end{array}\right)} \qquad (9)$$

In the case of a low pressure of n-hexane the overall rate equation per acid sites can be approximated by:

$$TOF = \frac{5.4 \times 10^{14} \exp\left(-114.5 \times 10^3 / RT\right)\left(P_{nC6} / p_{H2}\right)}{1 + 2.5 \times 10^3 \exp\left(-79 \times 10^3 / RT\right)\left(P_{nC6} / P_{H2}\right)} \qquad (10)$$

Conclusions

By measuring the rate of the n-hexane hydroisomerization reaction on Pt/HY-zeolite as a function of n-hexane pressure and fitting the results to a rate equation on the bifunctoinal isomerization scheme of Weisz, it was possible to simultaneously determine the equilibrium constant of n-hexane protonation and the rate of constant of isomerization of the resulting n-hexyl alkoxides. By repeating this procedure at different temperatures, the protonation energy ΔHpro, the activation energy of isomerization Eact,iso and corresponding preexponential factor could be determined. The measured values of ΔHpro equal to -79 kJ/mol whereas the value of Eact,iso equal to 119.7 kJ/mol. These values are agree well with the results of quantum-chemical calculations.

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دراسة حركية تفاعل ازمرة الحفاز للهكسان الاعتيادي

*عبد الحليم عبد الكريم, اميل رحمن و مها الحسني

*جامعة بغداد – كلية الهندسة – قسم الهندسة الكيماوية -بغداد-العراق

تم تحضير العامل المساعد 0.3wt%Pt/HY-zeolite بطريقة التحميل الرطب واستخدمت لازمرة الهكسان الاعتيادي. أجريت التجارب المختبرية بضغط جوي في منظومة ريادية تحتوي على مفاعل ذو الحشوة الثابتة و بدرجات حرارية تراوحت بين 240- 270 ° م و سرع فراغية 1-3 سا⁻¹ و النسب المولية للهيدروجين إلى الهكسان الاعتيادي 1-4.

تم اشتقاق المعادلة العامة لسرعة التفاعل بالاعتماد على ميكانيكية ثنائية الدالة. استخدمت البيانات المتوفرة في الأدبيات لحساب ثوابت التوازن لعملية الامتصاص وإزالة الهيدروجين.

ان قيمة طاقة تنشيط لتفاعل الازمرة هي 119.7 كيلو جول/مول في حين قيمة انثالبية تفاعل توليد البروتونات ـ 79 كيلو جول/ مول يمكن التعبير عن المعادلة العامة لسرعة التفاعل كالتالي:

$$TOF = \frac{5.4\times10^{14}\exp\left(-114.5\times10^3/RT\right)\left(P_{nC6}/P_{H2}\right)}{\left(\begin{array}{c}1+5\times10^{-10}\exp\left(44.2\times10^3/RT\right)P_{nC6}\\+19.6\exp\left(-73.8\times10^3/RT\right)\left(P_{nC6}/P_{H2}\right)\\+2.5\times10^3\exp\left(-5\times10^3/RT\right)\left(P_{nC6}/P_{H2}\right)\end{array}\right)}$$