Kinetic Study of Benzothiophene Hydrogenation Catalyzed by Ruthenium Complex

Oravan Sanguanruang* and Somsak Angdonka

Kinetic and mechanistic studies of benzothiophene hydrogenation were carried out by using $(PPh_3)_3RuCl_2$ as a catalyst with toluene as a solvent at 150ºC. The kinetic runs were performed at different concentrations of catalyst, benzothiophene, and hydrogen and at different temperatures. The reaction proceeds according to the rate law $r = k_{cat}[cat][H_2]$. Large negative values of $\Delta S^{\#}$ indicate a high degree of bond formation at the transition state. Dihydrobenzothiophene and ethylbenzene were obtained as the end products of the $(PPh_3)_3RuCl_2$ catalytic reaction at 200-250°C and a hydrogen pressure of 30 bar. It is proposed that the hydrodesulfurization of benzothiophene catalyzed by $(PPh_3)_3RuCl_2$ is hydrogenation prior to hydrogenolysis.

Key words: Hydrogenation, kinetics and ruthenium complex.

Materials Chemistry and Catalysis Research Unit, Department of Chemistry, Faculty of Science,
Chulalongkorn University, Patumwan, Bangkok 10330, Thailand.
**Correspondence to: e-mail: Oravan.s@chula.ac.th*

การศึกษาจลนพลศาสตร์ของปฏิกิริยาไฮโดรจิเนชันของเบนโซไทโอฟีนที่ถูกเร่งด้วยสารเชิงซ้อนรูทีเนียม

อรวรรณ สงวนเรือง และ สมศักดิ์ อ่างดอนคา (2548)
วารสารวิจัยวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย **30(1)**

การศึกษาทางจลนพลศาสตร์และกลไกการเกิดปฏิกิริยาไฮโดรจิเนชันของเบนโซไทโอฟีนโดยใช้ $(PPh_3)_3RuCl_2$ เป็นตัวเร่งปฏิกิริยาในตัวทำละลายทอลูอีนที่อุณหภูมิ 150 องศาเซลเซียส ทำการทดลองทางจลนพลศาสตร์โดยการแปรเปลี่ยนความเข้มข้นของคะตาลิสต์ เบนโซไทโอฟีน แก๊สไฮโดรเจนและที่อุณหภูมิต่างกัน ปฏิกิริยาดำเนินไปตามกฎอัตราเร็ว $r = k_{cat}[cat][H_2]$ ค่า $\Delta S^{\neq}$ เป็นลบมากแสดงถึงการเกิดพันธะที่สถานะทรานสิชัน ไดไฮโดรเบนโซไทโอฟีนและเอทิลเบนซีนเป็นผลิตภัณฑ์จากปฏิกิริยาคะตาไลสิซโดย $(PPh_3)_3RuCl_2$ ที่ 200-250 องศาเซลเซียส และความดันไฮโดรเจน 30 บาร์ ซึ่งแสดงว่าปฏิกิริยาไฮโดรดีซัลเฟอไรเซชันของเบนโซไทโอฟีนที่ถูกเร่งด้วย$(PPh_3)_3RuCl_2$ นั้น ปฏิกิริยาไฮโดรจิเนชันเกิดก่อนแล้วตามด้วยไฮโดรจิโนไลซิส

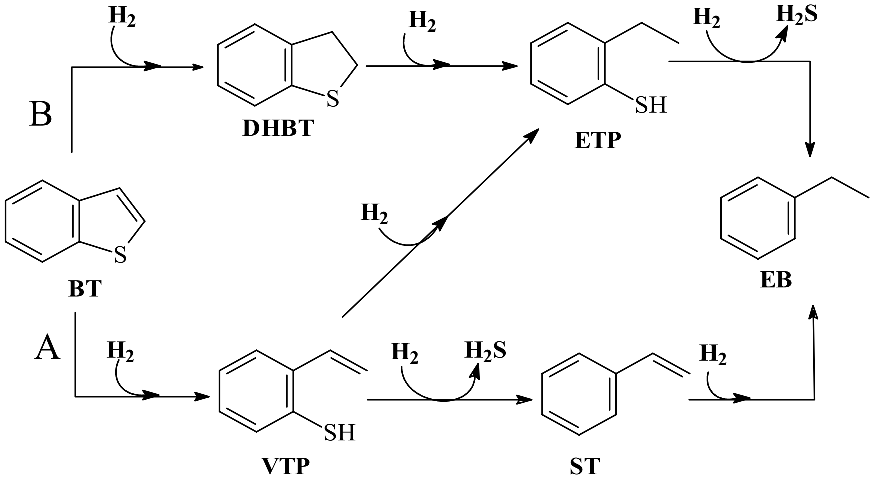
คำสำคัญ ปฏิกิริยาไฮโดรจิเนชัน จลนพลศาสตร์ สารเชิงซ้อนรูทีเนียม

INTRODUCTION

Heavy petroleum and coal derived liquids contain organic sulfur in varying levels. Organosulfur compounds found in petroleum are nonheterocycle and heterocycle such as thiols, sulfides, thiophenes and benzothiophenes (BT). The presence of sulfur acts as a poison to the metal catalysts used in the refining reaction causing catalytic cracking and reforming. Also, the polluted oxide (SO_x) is produced during combustion of the fuel, therefore sulfur compounds must be removed by hydrodesulfurization (HDS) as shown in equation (1)

$$C_xH_yS + 2H_2 \rightarrow C_xH_{y+2} + H_2S \qquad \ldots (1)$$

In general, hydrodesulfurization is carried out industrially in the heterogeneous phase. Alumina-supported Co-Mo and Ni-Mo(1-3) have been used as conventional catalysts in petroleum hydrotreatment. The mechanisms proposed for HDS of benzothiophenes involve either hydrogenolysis of the C-S bonds to give thiol followed by hydrogenation of the cleaved benzothiophene molecule (path A) or hydrogenation of the olefenic C=C bond prior to desulfurization (path B) to give ethyl benzene (EB)(4) (Scheme 1).



Scheme 1. The proposed reaction pathways for hydrodesulfurization of benzothiophene.

In order to understand the mechanism of the heterogeneous HDS, homogeneous model systems have been explored especially those of thiophenic substrates.(5,6) The types of reactions manifested by homogeneous organometallic compounds are also found on the surface of heterogeneous catalysts. Therefore the mechanistic information obtained from the homogeneous model can be applied to the surface counterparts.

Mechanisms of benzothiophene hydrodesulfurization using various catalysts (e.g. Rh, Ir and Ru complexes) are described in the literature.(7-9) Sanchez-Delgado and co-workers reported the catalytic activity of $(PPh_3)_3RuCl_2$ for the hydrogenation of benzothiophene. The reduction of sulfur heterocycle required 110 bar of H_2 and a temperature of ~170°C.(10) The observed kinetics were expressed by the equation: rate = k $[H_2]$[catalyst][benzothiophene]. The mechanism deduced from this rate law was not mentioned. They concluded that $(PPh_3)_3RuCl_2$ catalyst was more active than $(PPh_3)_3RhCl$ complex.

In the present paper, we disclose work on the kinetics and mechanism of hydrogenation of benzothiophene catalyzed by ruthenium complex. This study provides kinetic information which leads to better understanding of the mechanism involved in this reaction.

MATERIALS AND METHODS

All reactions and manipulations were performed under a nitrogen atmosphere by using Schlenk techniques or a glove bag. Reactions under the desired pressure of hydrogen were conducted with a stainless steel

Parr 4042 reactor (600 ml) equipped with controlled pressure and temperature. Reagent grade chemicals were used in this experiment. Tris(triphenylphosphine)ruthenium(II)chloride, triphenylphosphine, benzothiophene (Fluka, Switzerland) were used as received. Toluene (Labscan, Ireland) was dried over sodium benzophenone and distilled under nitrogen before use. GC analyses were performed on a Shimadzu 16A gas chromatograph. The chromatograph was equipped with a flame ionization detector and a 30 m. (0.25 mm *i.d.*, 0.25 μm film thickness) DB-WAX capillary column. GC/MS data were collected on a Varian Saturn 4D spectrometer.

Kinetic measurements

The reaction rates were determined as a function of change in the reaction conditions: concentrations of [$(PPh_3)_3RuCl_2$] catalyst, benzothiophene and hydrogen gas and reaction temperatures at a very early stage of the reaction. The reaction was followed by monitoring the appearance of dihydrobenzothiophene product as a function of time. The initial rates method was used for kinetic data analysis. It is reported that in the absence of added triphenylphosphine this catalyst can form dimers which complicate the nature of the reaction mechanism.(11,12) Therefore all experiments were carried out in the presence of triphenylphosphine.

General procedure

In a typical reaction, the appropriate amounts of $(PPh_3)_3RuCl_2$ dissolved in toluene, benzothiophene in toluene and triphenylphosphine were placed in a stainless steel autoclave in which a nitrogen atmosphere was present. The reaction volume was kept constant at 50.0 ml for every batch. The autoclave was sealed and the system was evacuated and pressurized with hydrogen up to 30 bar at room temperature. The reaction was heated to the required temperature by circulating thermostat liquid through a jacket around the reactor and stirred at 400 rpm. Samples of the solution were collected after 1 min. use. Additional sampling occurred after 2, 3, 6, and 9 hours of reaction time. The obtained solution was determined by GC and GC-MS analysis. Each run was repeated at least twice to ensure the reproducibility of the results.

The effect of the concentration of $(PPh_3)_3RuCl_2$ catalyst on the reaction rate

The experiments were carried out by varying the concentration of catalyst from 8.00×10^{-4} M to 13.50×10^{-4}M at 150°C. The concentration of benzothiophene was 8.00×10^{-2} M and hydrogen pressure was 30 bar. The procedure is explained in the general procedure section. The concentration of product versus time was then plotted.

The effect of the concentration of benzothiophene on the reaction rate

The experiments were carried out by using the concentration of catalyst at 8.00×10^{-4}M and varying the concentration of benzothiophene from 6.00×10^{-2} M to 12.00×10^{-2} M at 150°C and hydrogen pressure 30 bar. The procedure is described in the general procedure section. The concentration of product versus time was then plotted.

The effect of concentration of hydrogen gas on the reaction rate

The concentrations of catalyst and benzothiophene were fixed at 8.00×10^{-4} M and 8.00×10^{-2} M, respectively. The pressure of hydrogen gas was varied from 15 to 30 bar. The operation is explained in the general procedure section. The concentration of product versus time was then plotted.

The effect of hydrogenation temperature on the reaction rate

The hydrogenation temperature was investigated by fixing the concentrations of catalyst and benzothiophene at 8.00×10^{-4} M and 8.00×10^{-2} M, respectively. The reaction temperature was varied from 120 to 160°C and the operation is described in the general procedure section. The concentration of product versus time was then plotted.

The effect of temperature ≥ 200°C

The concentrations of catalyst and benzothiophene were fixed at 8.00×10^{-4} M and 8.00×10^{-2} M respectively. The reaction was carried out at hydrogen pressure of 30 bar, reaction temperatures at 200, 220 and 250°C and a reaction time of 72 hours. The operation is as described in the general procedure section.

RESULTS AND DISCUSSIONS

The kinetics of the hydrogenation of benzothiophene to dihydrobenzothiophene were studied by using $(PPh_3)_3RuCl_2$ as catalyst. The kinetic runs were carried out at various concentrations of catalyst, benzothiophene and hydrogen and at different temperatures. The measured value of DHBT was converted to molar concentration and the data were plotted as molar concentrations of DHBT as a function of time, yielding straight lines. Initial rates were then obtained from the corresponding slope.

The initial rate of hydrogenation of benzothiophene was found to be first-order dependent with respect to catalyst concentration, as confirmed by the plot of log r_i versus log [cat] which yielded a straight line with a slope of 1.1. No effect on the rate was detected on varying the benzothiophene concentration by the plot of log r_i *versus* log [benzothiophene concentration]. The result indicates that the hydrogenation rate is zero order with respect to benzothiophene concentration.

The variation of initial rates with hydrogen concentration indicates a first-order dependence with respect to hydrogen concentration as determined by the plot of log r_i *versus* log $[H_2]$, which yielded a straight line with a slope of 1.0. The complete data are listed in Table 1.

Table 1. Kinetic data for the hydrogenation of benzothiophene with $(PPh_3)_3RuCl_2$ catalyst.

Entry	10^4[Ru]	10^2[BT]	$10^3[H_2]$	T, °C	$10^6 r_i$, Ms^{-1}	k_{cat}, $M^{-1}s^{-1}$
1	8.00	8.00	4.05	150	1.10	0.340
2	9.50	8.00	4.05	150	1.33	0.345
3	11.00	8.00	4.05	150	1.51	0.339
4	12.00	8.00	4.05	150	1.67	0.344
5	13.50	8.00	4.05	150	1.90	0.348
6	8.00	6.00	4.05	150	1.10	0.341
7	8.00	10.00	4.05	150	1.10	0.340
8	8.00	12.00	4.05	150	1.11	0.342
9	8.00	8.00	3.41	150	0.94	0.344
10	8.00	8.00	3.60	150	0.97	0.339
11	8.00	8.00	3.82	150	1.05	0.343
12	8.00	8.00	4.05	120	0.96	0.140
13	8.00	8.00	4.05	130	1.00	0.202
14	8.00	8.00	4.05	140	1.05	0.278
15	8.00	8.00	4.05	160	1.30	0.431

Using the experimental rate law, we can write the following:

$$d[DHBT]/dt = k_{cat}[cat][H_2] \qquad \ldots (2)$$

The average value for the catalytic rate constant at 423 K was calculated from equation 2: $k_{cat} = 0.34 \pm 0.01\ M^{-1}s^{-1}$. The experimental rate found for ruthenium complex in toluene (equation 2) is identical to that for $[Rh(COD)(PPh_3)_2]PF_6$ in 2-methoxyethanol and 1,2 dichloroethane solvents,(7,8) (rate law = $d[DHBT]/dt = k_{cat}[Rh][H_2]$). The activity of the ruthenium complex in this experiment is higher than that observed for the Rh complex in 2-methoxyethanol as solvent ($k_{cat} = 1.24 \times 10^{-4}\ M^{-1}s^{1}$, 298 K). The Rh catalyst in 1,2 dichloroethane ($k_{cat} = 1.09 \times 10^{-2}\ M^{-1}s^{-1}$, 298 K) turns out to be more active than the Rh system in 2-methoxyethanol. It is shown that there is a marked effect of the solvent found in these two systems. The results mean that a coordinating solvent, such as 2-methoxyethanol, can compete with the benzothiophene substrate for the vacant coordination site and probably stabilize the unsaturated species through solvation of the catalysis. The involvement of 2-methoxyethanol can slow down the rate of the hydrogenation reaction. The solvent 1,2 dichloroethane coordinates poorly with the Rh complex, which explains the higher observed catalytic rate. In this work, toluene solvent was a poor coordinating solvent which is assumed to have no effect on the rate of reaction.

The effect of temperature on the rate constants was studied in the range of 393-433 K (120-160°C) for the concentration of catalyst at 8.00×10^{-4} M, benzothiophene at 8.00×10^{-2} M and dissolved hydrogen at 4.05×10^{-3} M.

The rate of reaction is affected by temperature, the most common behavior is observed by Arrhenius. The empirical expression is shown in equation 3.

$$k_{cat} = A \exp(-E_a/RT) \qquad \dots (3)$$

Thus a plot of ln k_{cat} *versus* $1/T$ allowed us to calculate the activation energy E_a (slope = $-E_a/R$)(Figure 1).

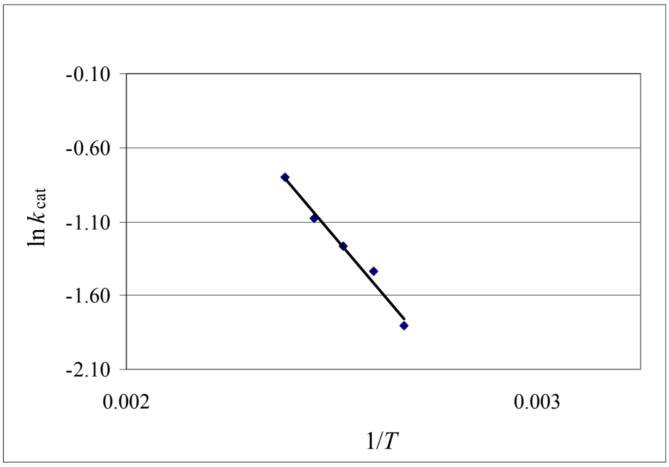


Figure 1. Plot of ln (k_{cat}) *versus* 1/*T*.

The values of enthalpy and entropy of activation were calculated from Eyring plot. The related parameters are shown in equation (4).

$$\ln(k_{cat}/T) = \ln(k_b/h) + \Delta S^{\neq}/R - \Delta H^{\neq}/RT \qquad \dots (4)$$

A plot of ln (k_{cat}/T) *versus* $1/T$ is shown in Figure 2. A straight line with slope and intercept corresponding to the activation enthalpy and activation entropy was obtained. Activation parameters for the hydrogenation of benzothiophene with $(PPh_3)_3RuCl_2$ as the catalyst are listed in Table 2.

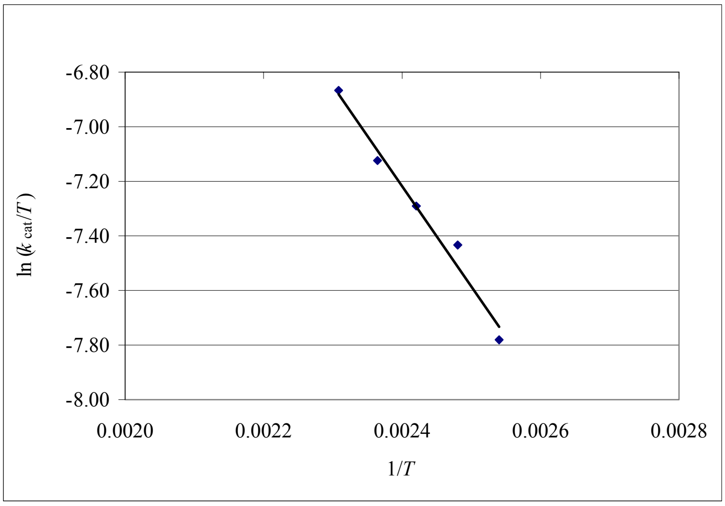


Figure 2. Plot of ln (k_{cat}/T) *versus* 1/*T*.

Table 2. Activation parameters for the hydrogenation of benzothiophene with $(PPh_3)_3RuCl_2$ catalyst.

Activation parameters	
E_a (k_{cal}/mol)	8.166 ± 0.001
k_{cat} (150 °C)($M^{-1}s^{-1}$)	0.34 ± 0.01
$\Delta H^{\neq}$ (k_{cal}/mol)	7.33 ± 0.02
$\Delta S^{\neq}$ (eu)	-44 ± 1
$\Delta G^{\neq}$ (k_{cal}/mol)	25.9 ± 0.1

Activation parameters $\Delta H^{\neq}$ and $\Delta S^{\neq}$ can provide information on the structure of the transition state complex. The values of $\Delta H^{\neq}$ and negative $\Delta S^{\neq}$ indicate that the transition state is formed early in the reaction. A large negative $\Delta S^{\neq}$ for the reaction implies a high degree of bond formation with little bond breakage.

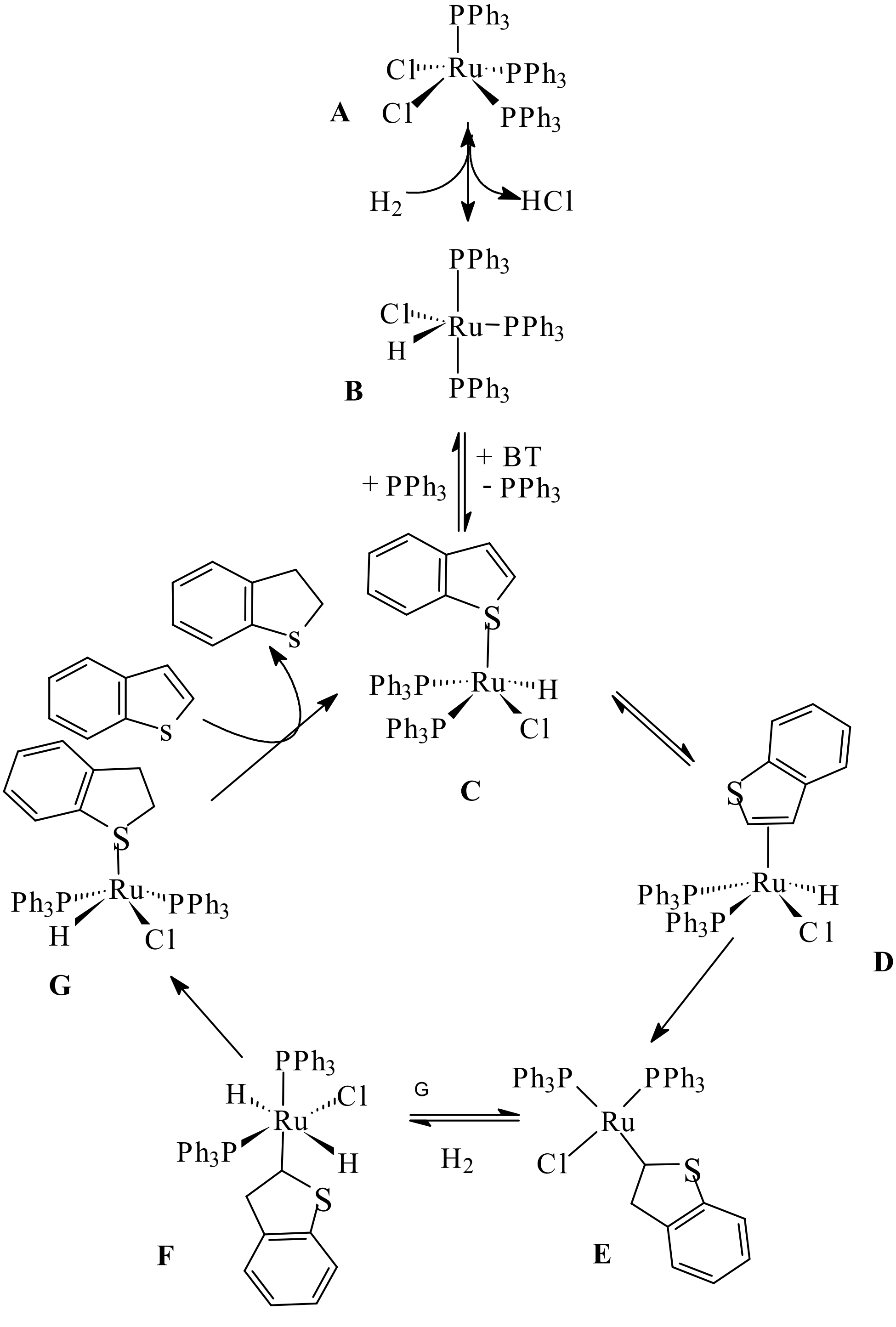
Characterization of product

Dihydrobenzothiophene is the product from hydrogenation catalyzed by $(PPh_3)_3RuCl_2$. GC-MS spectrum showed m/z = 136 which is the molecular mass of dihydrobenzothiophene.

The mechanism of benzothiophene hydrogenation

From rate law d[DHBT]/dt = k_{cat}[Ru][H_2] the reaction rate is first order with respect to both the catalyst and the hydrogen gas concentrations. The rate law results found in this experiment were similar to the one determined for the rhodium system in 2-methoxyethanol. It is suggested that the mechanisms for both catalysts are closely related. The mechanism is proposed in Scheme 2. $(PPh_3)_3RuCl_2$ catalyst is rapidly transformed into complex (B). Benzothiophene may approach the metal using either the sulfur atom or the $C_2 = C_3$ double bond or equilibrium between these two bonding modes.(13-15) The η^2-benzothiophene coordination mode is generally accepted to be the crucial one for the hydrogenation of the thiophenic ring.(16) This olefin-like species undergoes stepwise selective hydrogenation of the $C_2 = C_3$ double bond to yield hydrogenated product (G). Hydride migration has previously been proposed to take place onto C_2 or C_3 to produce 2-benzothienyl or a 3-benzothienyl complex respectively. On the basis of theoretical studies, including recent ab initio calculations, indications are that the C_2

atom of free benzothiophene has a greater negative charge than the C_3 atom and an intermediate (E) is most likely to occur. Oxidative addition of H_2 to complex (E) is a well-known process eventually occurring as complex (F). Transfer of the hydride to coordinated complex (F) generates complex (G). This complex reacts with benzothiophene and dissociates dihydrobenzothiophene to regenerate (C). It was found that the only product obtained from the kinetic study was dihydrobenzothiophene.



Scheme 2. Proposed mechanism of hydrogenation of benzothiophene catalyzed by $(PPh_3)_3RuCl_2$.

The effect of temperature ≥ 200°C

Hydrodesulfurization of benzothiophene catalyzed by $(PPh_3)_3RuCl_2$ was carried out at 200, 220 and 250°C while maintaining a hydrogen pressure of 30 bar and after 72 hours reaction time. The results were summarized in Table 3.

Table 3. Hydrodesulfurization of benzothiophene catalyzed by $(PPh_3)_3RuCl_2$ catalyst.

Temperature (ºC)	% conversion of benzothiophene	% DHBT	% ethyl benzene
200	70.1	51.1	7.8
220	79.6	54.4	11.6
250	89.4	58.3	21.3

In addition to the dihydrobenzothiophene obtained from the hydrogenation reaction, a small amount of ethyl benzene appears as a product at 72 hours reaction time. When the interaction of benzothiophene with hydrogen is allowed to proceed for a longer time, C–S bond rupture can occur. It is suggested that hydrodesulfurization of benzothiophene proceeds through hydrogenation of benzothiophene and then hydrogenolysis to give ethyl benzene.

The experimental data reveals % conversion of benzothiophene as well as the amounts of dihydrobenzothiophene and ethyl benzene increase at temperatures ≥ 200ºC. As the temperature increases above 200ºC, the percentage of ethyl benzene increases significantly. This means that hydrogenolysis can occur faster at higher temperature. Finally, it is concluded that the activity of the ruthenium catalyst increases with the increasing temperature.

CONCLUSIONS

Kinetic measurement of benzo-thiophene hydrogenation using $(PPh_3)_3RuCl_2$ catalyst was investigated. The reaction was carried out in a Parr Reactor with toluene as solvent. The kinetic runs were done at different concentrations of catalyst, benzothiophene and hydrogen and at difference temperatures. From experimental data, it is concluded that the rate of hydrogenation of benzothiophene is first-order with respect to the catalyst and hydrogen gas concentration. No effect on the hydrogenation rates was observed with varying concentration of benzothiophene. The reaction rate can be written as d/[DHBT]/dt = $k_{cat}[cat][H_2]$ and k_{cat} at 150ºC = 0.34 ± 0.01 $M^{-1}s^{-1}$. The activation parameters are $\Delta H^{\neq}$ = 7.33 ± 0.02 k_{cal}/mol, $\Delta S^{\neq}$ = -44 ± 1 eu and $\Delta G^{\neq}$ = 25.9 ± 0.1 k_{cal}/mol. Dihydrobenzothiophene is the major product of the hydrodesulfurization process at 150°C. This catalytic reaction is presumed to go through hydrogenation and then hydrogenolysis to give the ethyl benzene product. With the use of $(PPh_3)_3RuCl_2$ catalyst, the benzothiophene hydrodesulfurization gives 21.3 % of ethyl benzene at a temperature 250°C and 30 bar of hydrogen pressure.

ACKNOWLEDGMENTS

The authors wish to thank the Chemistry Department, Faculty of Science, Graduate School, Chulalongkorn University for financial support.

REFERENCES

1. Farag, H., Whitehurst, D. D., and Mochida, I. (1998) “Synthesis of Active Hydrodesulfurization Carbon-Supported Co-Mo Catalysts. Relationships Between Preparation Methods and Activity/ Selectivity”, *Ind. Eng. Chem. Res.* **37**, 3522-3530.
2. Girgis, M. J., and Gate, B. C. (1991) “Reactivities, Reaction Networks and Kinetics in High Pressure”, *Ind. Eng. Chem. Res.* **30**, 2021-2026.
3. Vrinat, M. L. (1983) “The Kinetics of the Hydrodesulfurization Process”, *Appl. Catal.* **6**, 137-141.

4. Curnow, O. J., Kampf, J. W., Curtis, M. D., Shen, J., and Basolo, F. (1994) "Kinetic and Structure Studies of the Reactions of Phosphorous Nucleophiles with the Sulfido Bimetallic Clusters", *J. Am.Chem. Soc.* **116**, 224-231.
5. Bianchini, C., Frediani, P., Herrera, V., Jimenez, M. V., Meli, A., Rincon, L., Sanchez-delgado, R. A., and Vizza, F. (1995) "Homogeneous Reaction of Thiophene with Transition Metals: A Modeling Approach for Elucidation of the Hydrodesulfurization Mechanism and an Effective Method for the Synthesis of Unusual Organosulfur Compounds", *J. Am. Chem. Soc.* **117**, 4333-4346.
6. Zhang, X., Dullaghan, C. A., Watson, E. T., Carpenter, G. B., and Swrigart, D. A. (1998) "Model for the Homogeneous Hydrodesulfurization of Benzothiophenes, Carbon-Sulfur Bond Cleavage, Hydrogenolysis, and Desulfurization Reactions Mediated by Coordination of the Carbocyclic Ring to Manganese and Ruthenium", *Organometallics* **17**, 2067-2075.
7. Sanchez-Delgaldo, R. A., Herrera, V., Rincon, L., Andriollo, A., and Martin, G. (1994) "Molecular Analogs of Surface Species 3. The Mechanism of the Regeoselective Homogeneous Hydrogenation of Benzothiophene by Use of $[Rh(COD)(PPH_3)_3]PF_6$ as the Catalyst Precursor Kinetic and Theoretical Study", O*rganometallics* **13**, 553-557.
8. Herrera, V., Fuentes, A., Rosales, M., Sanchez-Delgaldo, R. A., Bianchini, C., Meli, A., and Vizza, F. (1997) "Homogeneous Hydrogenation of Benzothiophene by use of Rhodium and Iridium Complexes as the Catalyst Precursors: Kinetic and Mechanistic Aspects", *Organometallics* **16**, 2465-2471.
9. Biachini, C., Meli, A., Moneti, S., Oberhauser, W., Vizza, F., Herrera, V., Fuentes, A., and Sanchez-Delgado, R. A. (1999) "Mimicking the HDS Activity of Ruthenium Based catalyst 2: The Hydrogenation of Benzothiophene to 2, 3-dihydrobenzothiophene", *J. Am. Chem. Soc.* **121**, 7071-7080.
10. Sanchez-Delgado, R. A., and Gonzalez, E. (1989) "Selective Homogeneous Hydrogenation of Benzothiophene Catalyzed by Ruthenium, Osmium, Rhodium and Iridium Complexes", *Polyhedron* **8**, 1431-1435.
11. Halpen, T. (1975) "Organotransition Metal Chemistry", Ishi, Y. and Tsutsi, M. (eds), Plenusm, New York, 1909.
12. Evans, D., Osborn, J. A., Jardine, F. H. and Wilkinson, G. (1965) Nature **208**, 1203.
13. Bianchini, C., and Meli, A. (1998) "In Aqueous-Phase Organometallic Catalyst-Concept and Application", *VCH Publisher,* Weinheim, Germany, 470.
14. Angelici, R. J. (1994) "In Encyclopedia of Inorganic Chemistry", *John Wiley*, New York, **3**, 1433.
15. Rauchfuss, T. B. (1991) "The Coordination Chemistry of Thiophene", *Prog. Inorg. Chem.* **39**, 259.
16. Angelici, R. J. (1988) "Heterogeneous Catalysis of the Hydrodesulfurization of Thiophenes in Petroleum: An Organometallic Perspective of the Mechanism", *Acc. Chem. Res.* **21**, 349-400.

Received: September 17, 2004
Accepted: January 31, 2005