TESTING THE RUTHENIUM(III) ACETYLACETONATE AND 1,2-BIS(DIPHENYLPHOSPHINO)ETHANE SYSTEM AS HOMOGENEOUS CATALYST IN THE HYDROLYSIS OF SODIUM BOROHYDRIDE

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ABSTRACT

TESTING THE RUTHENIUM(III) ACETYLACETONATE AND 1,2-BIS(DIPHENYLPHOSPHINO)ETHANE SYSTEM AS HOMOGENEOUS CATALYST IN THE HYDROLYSIS OF SODIUM BOROHYDRIDE

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Recent studies have shown that ruthenium(III) acetylacetonate is acting as homogeneous catalyst in the hydrolysis of sodium borohydride. Although trimethlyphosphite is found to be a poison for the catalytic hydrolysis of sodium borohydride, a longer observation of the reaction in the presence of ruthenium(III) acetylacetonate and 2 equivalent trimethylphosphite shows an unexpected enhancement in the catalytic activity after an induction period. The same rate enhancement is observed when 2 equivalent triphenylphosphine is added into the reaction solution. Addition of 1 equivalent 1,2-bis(diphenylphosphino)ethane, dppe, into the solution shows similarly a rate enhancement in the hydrolysis of sodium borohydride catalyzed by ruthenium(III) acetylacetonate. The effect of 1,2-bis(diphenylphosphino)ethane on the catalytic activity of ruthenium(III) acetylacetonate in the hydrolysis of sodium borohydride was studied by varying mole ratio of dppe / $Ru(acac)_3$, ruthenium concentration, substrate concentration and temperature. The highest enhancement in the rate of hydrolysis was obtained when 1 equivalent dppe was used and therefore, this mole ratio of dppe / $Ru(acac)_3$ was used in the further studies. The rate of the reaction was found to be first order in catalyst concentration and zero order in substrate concentration. From the evaluation of rate constant versus temperature data, the activation parameters for the hydrolysis of

sodium borohydride catalyzed by ruthenium(III) acetylacetonate plus 1 equivalent dppe were found to be Ea= 59 ± 2 kJ/mol, $\Delta H^{\neq}$ = 60 ± 1 kJ.mol^{-1} and $\Delta S^{\neq}$ = -50 ± 3 J.(mol.K)$^{-1}$. A series of control experiments were performed to characterize the active catalyst. However, the only useful information could be obtained by comparison of the UV-vis electronic absorption spectra taken from the solution during the catalytic reaction, is that, ruthenium(III) is reduced to ruthenium(II) in the course of reaction. It was concluded that a ruthenium(II) species is formed as a transient and may be the active catalyst in the reaction. After the reaction, the only ruthenium species isolated from the solution was the ruthenium(III) acetylacetonate.

Keywords: Ruthenium(III) Acetylacetonate, 1,2-bis(diphenylphosphino)ethane, Homogeneous Catalyst, Hydrolysis, Sodium Borohydride.

ÖZ

RUTENYUM(III) ASETİLASETONAT VE 1,2-BİS(DİFENİLFOSFİNO)ETAN'IN SODYUM BORHİDRÜR'ÜN HİDROLİZİNDE HOMOJEN KATALİZÖR OLARAK DENENMESİ

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Son çalışmalar, sodyum borhidrürün hidrolizinde rutenyum(III) asetilasetonatın homojen katalizör olduğunu göstermiştir. Trimetilfosfitin, sodyum borhidrürün katalitik hidrolizinde zehir etkisi yaptığı bulunmuş olmasına karşın, rutenyum(III) asetilasetonat ve 2 eşdeğer trimetilfosfitin varlığında gerçekleşen sodyum borhidrürün hidrolizinin uzun süreli gözlenmesi, bir bekleme süresinin ardından katalitik etkinlikte beklenmeyen bir artış olduğunu göstermektedir. Aynı hız artışı tepkime çözeltisine 2 eşdeğer trifenilfosfin eklendiğinde de gözlenmektedir. Çözeltiye 1 eşdeğer 1,2-bis(difenilfosfino)etan (dppe) eklenmesi, rutenyum(III) asetilasetonat tarafından katalizlenen sodyum borhidrürün hidrolizinin hızında benzer bir artış göstermektedir. 1,2-bis(difenilfosfino)etanın, rutenyum(III) asetilasetonatın sodyum borhidürürün hidrolizindeki katalitik etkinliğine etkisi, dppe / $Ru(acac)_3$ mol oranı, rutenyum derişimi, tepken derişimi ve sıcaklık değiştirilerek çalışıldı. Hidroliz hızındaki en yüksek artış dppe / $Ru(acac)_3$ mol oranı 1 olduğunda elde edildi ve bundan sonraki çalışmalarda bu mol oranı kullanıldı. Tepkime hızının katalizör derişimine göre birinci dereceden, tepken derişimine göre sıfırıncı dereceden olduğu bulundu. Hız sabitine karşı sıcaklık verilerinin değerlendirilmesinden, rutenyum(III) asetilasetonat ve 1 eşdeğer dppe tarafından katalizlenen sodyum borhidrürün hidrolizi için aktivasyon parametreleri bulundu: Ea = 59 ± 2 kJ/mol, $\Delta H^{\neq}$ = 60 ± 1

$kJ.mol^{-1}$ and $\Delta S^{\neq} = -50 \pm 3$ $J.(mol.K)^{-1}$. Etkin katalizörü tanımlamak amacıyla bir dizi kontrol deneyi yapıldı. Ancak kullanılabilir tek bilgi, katalitik tepkime süresince alınan morötesi-görünür bölgesi elektron soğurma spektrumlarından elde edildi. Spektrumların karşılaştırılmasından tepkime sırasında rutenyum(III) iyonunun bir rutenyum(II) türüne indirgendiği anlaşıldı. Sonuçta bir ara ürün olarak oluşan rutenyum(II) kompleksi, etkin katalizör olabilir. Tepkime sonrasında çözeltiden elde edilebilen tek rutenyum türü, rutenyum(III) asetilasetonattır.

Anahtar Kelimeler: Rutenyum(III) Asetilasetonat, 1,2-bis(difenilfosfino)etan, Homojen Katalizör, Hidroliz, Sodium Borhidrür

To my family

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CHAPTER 1

INTRODUCTION

Global warming is one of the most important reasons that the world should change its energy policy from fossil fuels to renewable and clean sources. From the beginning of industrialization, humankind has been consuming natural resources without thinking about the environmental impact and possible consequences of their exhaustion.[1] Current CO_2 concentration in the atmosphere is 30% above the level of the pre-industrial era.[2] Global warming, due to increase in CO_2 concentration, causes hundreds of deaths in warm climate countries, increasing levels of sea water worldwide which threatens seaside cities, and numerous other natural disasters such as floods, hurricanes, forest fires, and so on.[1] Environmental needs lead people to consider about new energy sources to reduce CO_2 emission. The principle drivers behind a sustainable energy vision of the future centre on the need to: (1) reduce global carbon dioxide emissions and improve local air quality, (2) ensure security of energy supply and move towards the use of sustainable local energy problems, and (3) create a new industrial and technological energy base, crucial for future economic prosperity.[3]

In order to meet the demand for the clean energy, there is a rapid improvement in different technologies such as solar energy, wind power, hydro power, biomass energy, geothermal energy, tidal energy and wave power. The main problem with those technologies is that energy produced from these sources is difficult to store and transport. It is obvious that an energy carrier is needed for all of these energy sources which will be hydrogen.[1]

Hydrogen exhibits the highest heating value per mass of all chemical fuels. Furthermore, hydrogen is regenerative and environmentally benign. However, it is just an energy carrier and, although it is the most abundant element in the universe, it has to be produced, since on earth it only occurs in the form of water and hydrocarbons.[4] The intrinsic properties and behavior of hydrogen storage materials depend upon the precise nature of the interactions of hydrogen with the host material. There are several types of such interactions: (1) physical adsorption of H_2 molecules on the surface (exterior or interior) of the material, (2) chemical adsorption of hydrogen by the material (and concomitant hydrogen dissociation) with the formation of chemical bonds, and (3) the formation of 'chemical hydrides' characterized by distinct chemical covalent bonding.[3]

As a new fueling concept, it can be suggested that the chemical hydrides ($NaBH_4$, KBH_4, LiH, MgH_2) act as new fuel source supplying hydrogen at normal temperature.[5] Chemical hydrides are very reactive toward hydrolysis in water, which results in generating large amount of hydrogen gas. Among these chemical hydrides, it was proposed that sodium borohydride ($NaBH_4$) would be a potential reducing and hydrogen-generating agent as it liberates 4 moles of hydrogen per mole of compound at room temperature.[6]

$$\mathrm{NaBH_4}(aq) + 2\mathrm{H_2O(l)} \xrightarrow{\text{catalyst}} \mathrm{NaBO_2}(aq) + 4\mathrm{H_2(g)} \qquad (1.1)$$

Generating H_2 from the catalytic hydrolysis of sodium borohydride in aqueous solution has many advantages: (1) $NaBH_4$ solutions are nonflammable, (2) $NaBH_4$ solutions are stable in air for months, (3) H_2 generation only occurs in the presence of selected catalysts, (4) the only other product in the gas stream is water vapor, (5) reaction products are environmentally benign, (6) H_2 generation rates are easily controlled, (7) volumetric and gravimetric H_2 storage efficiencies are high, (8) H_2 can be generated even at $0^{o}C$.[7] In addition, although the hydrolysis

reactions of other chemical hydrides are not reversible, a study by Kojima et al. describes a concept in order to convert $NaBO_2$ back to $NaBH_4$ using coke or methane.[8]

$$NaBO_2 + 2MgH_2 \longrightarrow NaBH_4 + 2MgO \qquad (1.2)$$

Since the hydrolysis of sodium borohydride is known to be an acid catalyzed reaction, the initial rate of hydrogen generation by hydrolysis of $NaBH_4$ decreases with the increasing pH of the solution caused by the formation of strongly basic metaborate ion.[6]

In addition to acidic medium[9] and elevated temperature[10], the rate of hydrolysis of $NaBH_4$ can be also accelerated by catalyst[11]. A catalyst is defined as a substance which increases the rate at which a chemical reaction approaches equilibrium, without being consumed in the process[12]. The effect of a catalyst may be shown both as a potential-energy profile and as an Arrhenius diagram: the latter makes it plain that the effect of a catalyst is either to increase the rate at a given temperature or to decrease the temperature at which the reaction achieves a given rate. It must be emphasized that lowering of the activation energy is a fundamental principle of catalysis and applies to all forms of catalysis: homogeneous, heterogeneous and enzymatic[12].

The catalyst may be added to the reaction medium in a different form, usually in the form of catalyst precursor which has to be converted into the active catalyst. During the catalytic cycle the catalyst may be present in several intermediate at molecular level. An active catalyst will pass a number of times through this cycle of states; in this sense the catalyst remains unaltered at the end of a catalytic cycle. The number of times that a catalyst goes through this cycle is known as the turnover number. The turnover number (TON) is the total number of substrate

molecules that a catalyst molecule converts into product molecules. The turnover frequency (TOF) is the turnover number in a certain period of time.[13]

The first study on catalytic hydrolysis of sodium borohydride was performed by Schlesinger using platinum and rhodium salts as catalyst,[14] followed by Pecsok,[15] L.Brown,[16] C.Brown (iron, ruthenium, palladium, osmium, iridium, and platinum salts),[17] Stockmayer,[18] Davis,[19,20] Mesmer,[21] Gardiner,[22] Sen (nickel, Raney nickel, and bulk cobalt),[23] Amendola (bulk ruthenium),[24] Kojima (mixed metal/metal oxides such as Pt-$LiCoO_2$),[25, 26, 27] Hanxi (nickel boride),[28] Lee,[29] Wu,[30, 31] Kim,[32] Yang[33] (filamentary nickel-cobalt). All of these catalysts used in hydrolysis of sodium borohydride are bulk metals and they act as heterogeneous catalysts[34] which has limited surface area restricting the catalytic activity.

In heterogeneous catalysis a phase boundary separates the catalyst from the reactants. For catalysis to occur, there must be a chemical interaction between the catalyst surface and the reactants-product system, but this interaction must not change the chemical nature of the catalyst except at the surface. The existence of a surface interaction, which does not penetrate into the interior of the solid, can be the reason of the concept of compatibility between catalyst, reactants, and products.[12] A good catalyst needs to adsorb the reactant molecules strongly enough for them to react, but not so strongly that the product molecules stick more or less permanently to the surface. The major advantage of heterogeneous catalysts is the ease of separation of the catalyst from reaction mixture at the end of the reaction. This eliminates or minimizes the need for additional work-up procedures which can often be expensive and can lead to generation of large volumes of waste, which is often toxic.

Since the limited surface area of a heterogeneous catalyst reduces the catalytic activity, the use of metal nanoparticles with large surface area provides a potential route to increase the catalytic activity.[35] For that reason, water dispersible

ruthenium(0) nanoclusters were used and it was shown that they are highly active catalyst in the hydrolysis of sodium borohydride.[36] The ruthenium(0) nanoclusters have been prepared from the reduction of $RuCl_3$ by sodium borohydride in the presence of acetate ion as stabilizer.[36] Since chloride anions could act as stabilizer in addition to acetate, it was considered that a precursor complex having an anionic ligand which would act as stabilizer can be used for the formation of ruthenium(0) nanoclusters from its reduction. For this purpose ruthenium(III) acetylacetonate was used as precursor to provide free acetylacetonate which would act as stabilizer for the ruthenium(0) nanoclusters generated from reduction in aqueous solution. Although it was observed that ruthenium(III) acetylacetonate can not be reduced by sodium borohydride, ruthenium(III) acetylacetonate was found to be an active catalyst already in its present form for the hydrolysis of sodium borohydride in aqueous solution.[37]

Homogeneous catalysis refers to a catalytic system in which the substrates for a reaction and the catalyst components are brought together in one phase, most often the liquid phase.[13] Even a small change in the coordination sphere of the metal ion can cause a considerable change in activity and selectivity of the catalyst. That the reaction occurs in homogeneous solutions also facilitates the study of the preliminary reaction steps involved in the catalytic mechanism. Changing the phosphine ligand or metal center may allow the isolation of metastable intermediate complexes, if not the active catalyst, which can provide information on the nature of the active catalyst. One of the disadvantages of homogeneous catalysis is that the catalyst remains in the medium together with product and unreacted substrate and its recovery is usually difficult. Ideally, one would prefer heterogeneous catalyst with the reactivity and selectivity of the homogeneous one. The present thrust in homogeneous catalysts is not only to increase their reactivity and by tailoring the ligands to attempt to promote selectivity in desired reaction, but also to render them heterogeneous for convenience in use by attaching them to a surface, hopefully without loss of reactivity or selectivity.[38]

A poison is the substance that stops the catalytic reaction and may kill the catalyst. During the study with ruthenium(III) acetylacetonate as catalyst in the hydrolysis of sodium borohydride, some poisoning experiments were performed in order to determine whether the catalyst is homogeneous or heterogeneous. For that purpose, trimethylphoshite was used as poison. As it can be seen from the plot in Figure 1.1, when the mole ratio of $P(OCH_3)_3$ /$Ru(acac)_3$ is exactly 1.0 the catalytic reaction is ceased. This has been considered as a compelling evidence for the catalyst being homogeneous.[37]

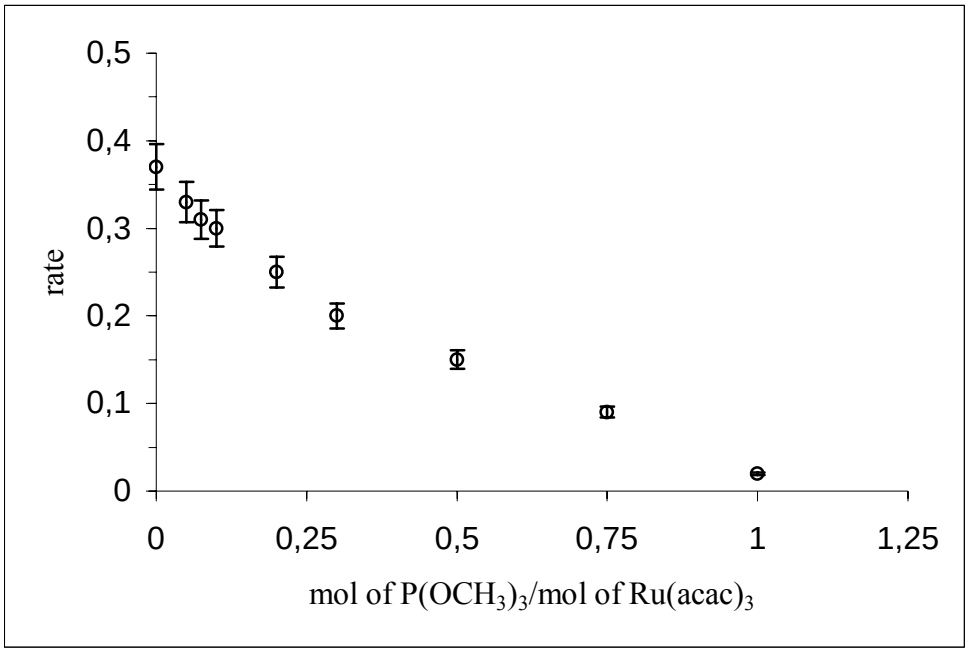

Figure 1.1. Plot of the relative rate versus the moles of $P(OCH_3)_3$/the moles of $Ru(acac)_3$ in the hydrolysis of sodium borohydride[37].

After the observation of the poisoning effect of $P(OCH_3)_3$ on ruthenium(III) acetylacetonate catalyst, an unexpected catalytic activity was observed upon waiting for a longer time after the addition of the poison trimethylphosphite into the reaction solution of $Ru(acac)_3$ and sodium borohydride. As shown in Figure 1.2, after a certain period of time, which will be referred as induction period hereafter, a sudden, huge increase in the rate of hydrogen generation was observed: A new catalyst must be formed from trimethylphosphite and ruthenium(III)acetylacetonate, which is obviously much more active than the ruthenium(III) acetylacetonate catalyst itself. It was of great interest whether this unexpected catalytic activity is unique for the trimethylphosphite or can be extended to the other phosphine ligands including the phenylphosphines. Of particular importance is the finding that the highest catalytic activity is obtained when two equivalent trimethylphosphite per ruthenium is used. This finding implies that the active catalyst might carry two phosphine ligands, presumably in two cis positons in the pseudo-octahedral coordination sphere of ruthenium.[39] Consequently, the use of one equivalent of a diphosphine chelate ligand will prove that the active catalyst has two phosphorous atoms in two cis positions. Since bis(diphenylphosphino)alkane (methane, ethane, propane…) are readily available and have widely been employed in tailoring the catalysis, we have decided to use 1,2-bis(diphenylphosphino)ethane, dppe, to test our hypothesis. However, a pre-examination had to be performed to ensure that the phenylphosphine is also as active as the trimethylphosphite in the hydrolysis of sodium borohydride.

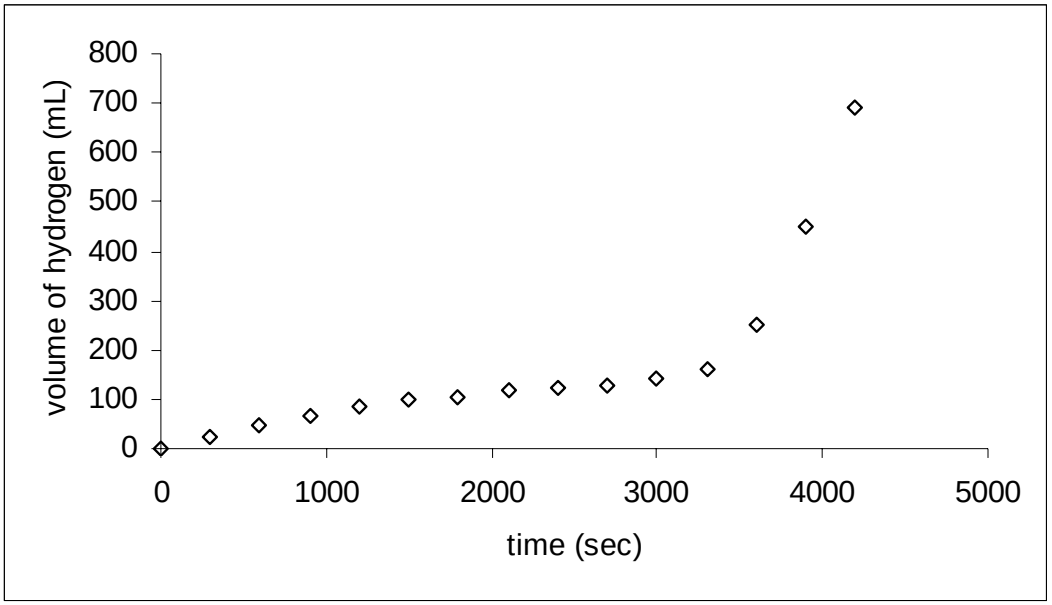

Figure 1.2. Plot of the volume of hydrogen generated versus time for the hydrolysis of sodium borohydride when [$NaBH_4$] = 150 mM, [$Ru(acac)_3$] = 2 mM, [$P(OMe)_3$]= 4 mM, T = 25 °C

A test experiment was performed starting with 2 mM ruthenium(III) acetylacetonate and 4 mM triphenylphosphine for the hydrolysis of 150 mM $NaBH_4$ solution at 25 ºC. The reaction was followed by measuring the amount of hydrogen generated from the hydrolysis of sodium borohydride versus time (Figure 1.3.). This plot shows, similar to trimethylphoshite, a sudden, huge increase in the reaction rate after an induction time of about 0.5 h. This indicates the formation of a new catalyst comprising triphenylphosphine and ruthenium(III) acetylacetonate.

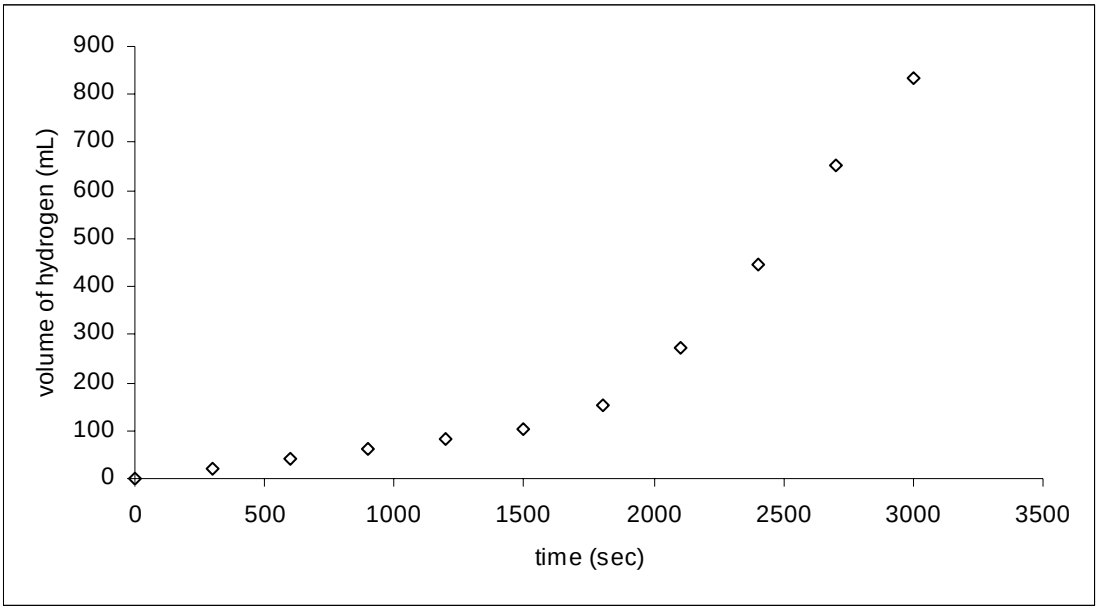

Figure 1.3. Plot of the volume of hydrogen generated versus time for the hydrolysis of sodium borohydride when [$NaBH_4$] = 150 mM, [$Ru(acac)_3$] = 2 mM, [PPh_3] = 4 mM, T = 25 ºC

Having observed that also the addition of phenylphosphines increases the catalytic activity of ruthenium(III) acetylacetonate in the hydrolysis of sodium borohydride, we could start a study to test the hypothesis that whether the use of one equivalent of a chelate ligand will enhance the catalytic activity of the same system.

This study aims the use of 1,2-bis(diphenylphosphino)ethane, dppe, as promoter to enhance the catalytic activity of ruthenium(III) acetylacetonate in the hydrolysis of sodium borohydride. Kinetics of the catalytic hydrolysis of sodium borohydride will be studied as well.

CHAPTER 2

EXPERIMENTAL

2.1. Materials

Ruthenium(III) acetylacetonate, $Ru(acac)_3$, (97 %), sodium borohydride, $NaBH_4$, (98%), trimethylphosphite, $P(OCH_3)_3$, triphenylphoshine, PPh_3, and 1,2-bis(diphenylphosphino)ethane, dppe, were purchased from Aldrich®, and tetrahydrofuran, THF, dichloromethane, DMF, and hexane were purchased from Merck®. All glassware and Teflon-coated magnetic stir bars were cleaned with acetone, followed by copious rinsing with distilled water before drying at 150 °C in oven for a few hours.

2.2. Equipment

The experimental setup used for performing the hydrolysis of sodium borohydride and measuring the hydrogen gas generated from the reaction consists of a 75 mL jacketed reaction flask containing a Teflon-coated stir bar placed on a magnetic stirrer (Heidolph MR-301) and thermostated to 25.0±0.1 °C by circulating water through its jacket from a constant temperature bath (RL6 LAUDA water bath). Then, a graduated glass tube (50 cm in height and 2.5 cm in diameter) filled with water was connected to the reaction flask to measure the volume of the hydrogen gas to be evolved from the reaction (Figure 2.1).

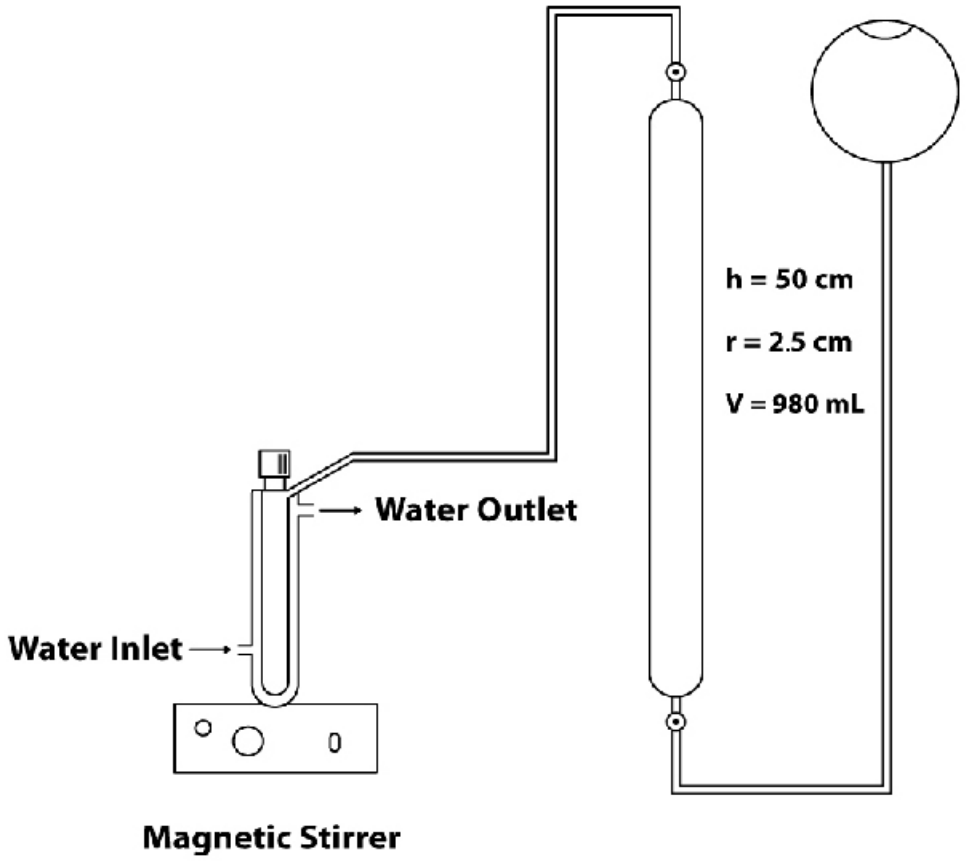

Figure 2.1. The experimental setup used in the measurement of the volume of hydrogen generated from the hydrolysis of sodium borohydride.

2.3. Self Hydrolysis of Sodium Borohydride

In order to measure the rate of hydrogen generation from the self hydrolysis of sodium borohydride, 284 mg (7.5 mmol) sodium borohydride was dissolved in 50 mL water and the solution was transferred into the reaction flask thermostated at 25.0 ± 0.1 °C. The experiment was started by closing the reaction flask and

turning on the stirring at 1000 rpm simultaneously. The volume of hydrogen gas generated was recorded every 5 minutes.

2.4. Catalytic Activity of Ruthenium(III) Acetylacetonate in the Hydrolysis of Sodium Borohydride

The catalytic activity of ruthenium(III) acetylacetonate in the hydrolysis of sodium borohydride was determined by measuring the rate of hydrogen generation. Firstly, 41 mg $Ru(acac)_3$ was dissolved in 5 mL THF and added into 45 mL aqueous $NaBH_4$ solution. The initial concentrations of $NaBH_4$ and $Ru(acac)_3$ were 150 and 2 mM, respectively. The experiment was started by closing the reaction flask and turning on the stirring at 1000 rpm simultaneously. The volume of hydrogen gas evolved was measured by recording the displacement of water level in every 5 minutes.

2.5. Catalytic Activity of Ruthenium(III) Acetylacetonate and Trimethylphosphite System in the Hydrolysis of Sodium Borohydride

A stock solution of $P(OCH_3)_3$ (100 mM) in THF was prepared by dissolving 1.18 mL $P(OCH_3)_3$ (MW = 124.08 g/mol, d = 1.052 g/mL) to 100 mL THF. For the preparation of $P(OCH_3)_3$ / $Ru(acac)_3$ solution with $P(OCH_3)_3$ / $Ru(acac)_3$ ratio of 1, 2, 3 or 4, an aliquot of the stock solution (1, 2, 3, or 4 mL, respectively) was diluted to 5 mL by adding THF. For each ratio of $P(OCH_3)_3$ / $Ru(acac)_3$; 41 mg $Ru(acac)_3$ was dissolved in THF solution containing $P(OCH_3)_3$. Then the solution was transferred into the reaction flask containing 284 mg $NaBH_4$ dissolved in 45 mL water and thermostated at 25.0 ± 0.1 °C. The initial concentration of $Ru(acac)_3$ in the reaction mixture was 2 mM and concentration of $P(OCH_3)_3$ was 2, 4, 6, and 8 mM, respectively. The reaction was started by closing reaction flask and turning on the stirrer at 1000 rpm simultaneously. The volume of hydrogen gas generated was recorded every 5 minutes.

2.6. Catalytic Activity of Ruthenium(III) Acetylacetonate and Triphenylphosphine System in the Hydrolysis of Sodium Borohydride

A stock solution of PPh_3 (100 mM) in THF was prepared by dissolving 2.65 g PPh_3 (MW = 262.29 g/mol, 99%) in 100 mL THF. For the preparation of PPh_3 / $Ru(acac)_3$ solution with PPh_3 / $Ru(acac)_3$ ratio of 2, 2 mL of stock solution was diluted to 5 mL with THF and 41 mg $Ru(acac)_3$ was dissolved in it. Then the solution was transferred into the reaction flask containing 284 mg $NaBH_4$ dissolved in 45 mL water and thermostated at 25.0 ± 0.1 °C. The initial concentrations of PPh_3 and $Ru(acac)_3$ in 50 mL solution were 4 and 2 mM, respectively. The reaction was started by closing reaction flask and turning on the stirrer at 1000 rpm simultaneously. The volume of hydrogen gas evolved was measured by recording the displacement of water level in every 5 minutes.

2.7. Catalytic Activity of Ruthenium(III) Acetylacetonate and 1,2-bis(diphenylphosphino)ethane System in the Hydrolysis of Sodium Borohydride

A stock solution of dppe (100 mM) in THF was prepared by dissolving 4.00 g dppe (MW = 398.43 g/mol, 97%) in 100 mL THF. For the preparation of dppe / $Ru(acac)_3$ solutions with dppe / $Ru(acac)_3$ ratio of 0.5, 1, 1.5, 2, or 2.5, an aliquot of the stock solution (0.5, 1, 1.5, 2, or 2.5 mL, respectively) was diluted to 5 mL with THF. For each ratio of dppe / $Ru(acac)_3$, 41 mg $Ru(acac)_3$ was dissolved in THF solution containing dppe. Then the solution was transferred into the reaction flask containing 284 mg $NaBH_4$ dissolved in 45 mL water and thermostated at 25.0 ± 0.1 °C. The initial concentration of $Ru(acac)_3$ in the reaction mixture was 2 mM and concentration of dppe was 1, 2, 3, 4, 5 mM, respectively. The reaction was started by closing reaction flask and turning on the stirrer at 1000 rpm simultaneously. The volume of hydrogen gas generated was recorded every 5 minutes.

2.8. Kinetic Study of Ruthenium(III) Acetylacetonate and 1,2-bis(dipheynylphosphino)ethane System Catalyzed Hydrolysis of Sodium Borohydride

The kinetics of the hydrolysis of $NaBH_4$ catalyzed by $Ru(acac)_3$ and dppe system was studied depending on substrate concentration, catalyst concentration and the temperature.

Initially, $NaBH_4$ concentration was held constant at 450 mM and $Ru(acac)_3$ concentration was varied in the range of 1, 1.5, 2, 2.5, 3, 3.5 and 4 mM, by holding dppe / $Ru(acac)_3$ ratio at 1, at 25.0 ± 0.1 °C. The hydrogen generation was measured for each set by recording the water level in graduated glass tube, which is connected to the reaction flask, in every 2 minutes.

Then, $Ru(acac)_3$ concentration was held constant at 2 or 3 mM, by keeping dppe / $Ru(acac)_3$ ratio at 1, while $NaBH_4$ concentration was varied in the range of 300, 600, 900, 1200 and 1500 mM at 25.0 ± 0.1 °C. Hydrogen generation was measured for each set by recording the water level in graduated glass tube, which is connected to the reaction flask, in every 2 minutes.

Finally, the catalytic hydrolysis of $NaBH_4$ in the presence of $Ru(acac)_3$ / dppe system with a $Ru(acac)_3$ concentration of 2 mM and a dppe / $Ru(acac)_3$ ratio of 1 was performed keeping $NaBH_4$ and $Ru(acac)_3$ / dppe system concentrations constant (450 mM and 2 mM respectively) at various temperatures in the range of 20, 25, 30, 35, and 40 °°C in order to obtain the activation energy (E_a), enthalpy of activation ($\Delta H^{\neq}$) and entropy of activation ($\Delta S^{\neq}$).

2.9. Catalytic Lifetime of Ruthenium(III) Acetylacetonate

The catalytic lifetime of $Ru(acac)_3$ / dppe system in the hydrolysis of sodium borohydride was determined by measuring the total turnover number (TTO). Such a lifetime experiment was started with a 50 mL solution containing 2 mM $Ru(acac)_3$ (dppe/ Ru = 1), and 450 mM $NaBH_4$ at 25.0± 0.1 °C.

When the conversion exceeded 75%, more $NaBH_4$ was added and the reaction was continued in this way until hydrogen gas evolution was slowed down to the self hydrolysis level.

2.10. UV-visible Spectroscopic Measurements

The hydrolysis of sodium borohydride catalyzed by $Ru(acac)_3$ / dppe system was followed by taking the UV-visible absorption spectra on a Varian Cary 100 Bio UV-visible Spectrophotometer. The catalytic hydrolysis of sodium borohydride was started with 2 mM $Ru(acac)_3$ (dppe / Ru = 1) and 450 mM $NaBH_4$ in 50 mL H_2O-THF (9:1) solution at 25.0 ± 0.1 °C. During the hydrolysis, more sodium borohydride was added to the solution to keep the reaction alive. Every 10 minutes, 50 μL sample was taken by using a micropipette and diluted to 3 mL with $NaBH_4$ solution (450 mM) in H_2O-THF (9:1). The UV-visible spectrum of the diluted solution was taken immediately.

In addition, 2mM $Ru(acac)_3$ solution was prepared in 50 mL H_2O-THF (9:1) to take UV-visible spectra of $Ru(acac)_3$ solution in the presence or absence of 450 mM $NaBH_4$.

2.11. Attempts for Crystallization

In order to crystallize the active catalyst, firstly 50 ml H_2O-THF(9:1) solution including 150 mM $NaBH_4$, 2mM Ru(acac)3 and 1 equivalent dppe was prepared and the reaction was started by closing reaction flask and turning on the stirrer at 1000 rpm simultaneously. After 1 hour, the reaction solution was put into an extraction funnel. Dichloromethane (50 ml) was added to the extraction funnel as organic phase. Then we separated organic phase from the water phase which included $NaBH_4$. A solid residue was obtained after evaporating organic solvent by vacuum. Then the solid residue was dissolved in 10 mL dichloromethane/n-hexane mixture The solution was cooled down to -35 °C and left for 10 days at this temperature. Unfortunately, the only crystal obtained was of the starting material ruthenium(III) acetylacetonate.

CHAPTER 3

RESULTS AND DISCUSSION

3.1. Self Hydrolysis of Sodium Borohydride

The reason why the hydrolysis of sodium borohydride should be catalyzed is that the rate of hydrogen gas generation from the self hydrolysis of sodium borohydride is very low. Figure 3.1 shows the plot of hydrogen volume generated from the hydrolysis of sodium borohydride (150 mM) solution versus time at 25 °C. It can be seen that only 150 mL of hydrogen is generated in 2.5 hours from uncatalyzed hydrolysis of sodium borohydride. Although the self hydrolysis of sodium borohydride is relatively slow, but the amount of hydrogen generated from the self hydrolysis is not negligible. One has to take it into account for the evaluation of hydrogen volume versus time data in the catalyzed reaction. In all the experiments involving the catalytic hydrolysis of sodium borohydride, the hydrogen volume versus time data will be corrected by subtracting the volume of hydrogen generated from the self hydrolysis of sodium borohydride in the same time interval.

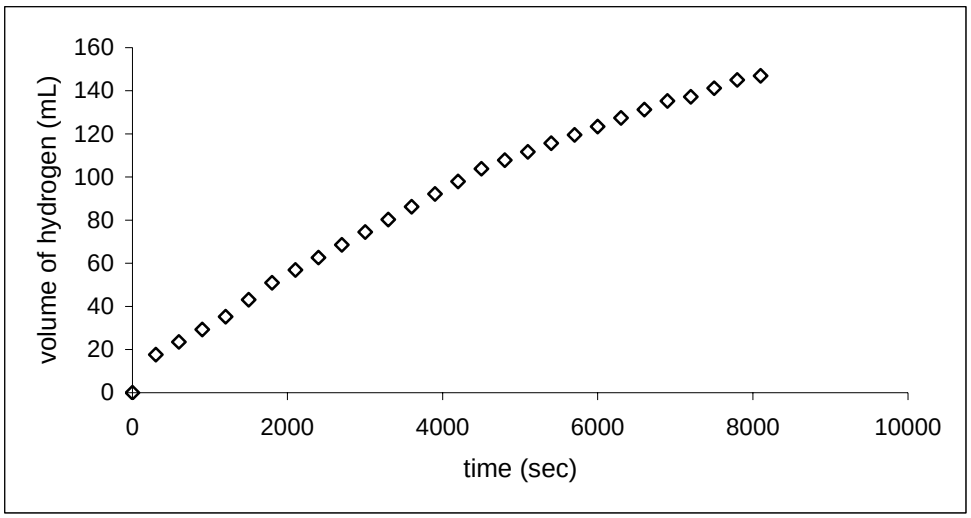

Figure 3.1 Plot of hydrogen volume versus time in the self hydrolysis of sodium borohydride. [$NaBH_4$] = 150 mM, T = 25 ºC.

3.2. Ruthenium(III) Acetylacetonate: A Homogeneous Catalyst in the Hydrolysis of Sodium Borohydride

It has been shown that ruthenium(III) acetylacetonate acts as catalyst in the hydrolysis of sodium borohydride[37]. The volume of hydrogen versus time plot for hydrogen generation from the hydrolysis of sodium borohydride catalyzed by ruthenium(III) acetylacetonate is given together with self hydrolysis of sodium borohydride in Figure 3.2.

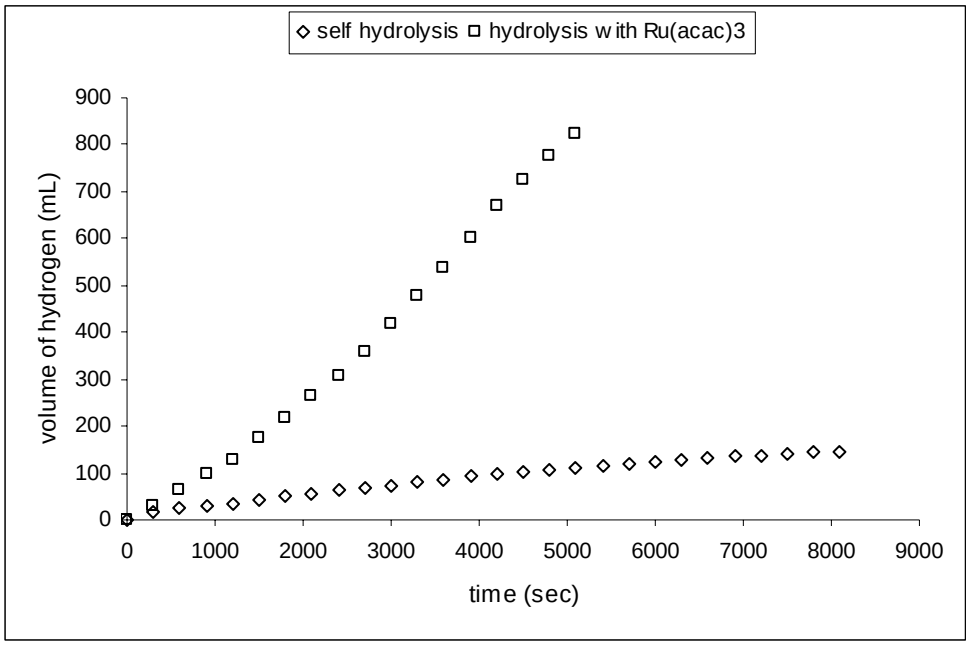

Figure 3.2 Plots of hydrogen volume versus time for the self hydrolysis of sodium borohydride and hydrolysis of sodium borohydride catalyzed by $Ru(acac)_3$. $[NaBH_4]$ = 150 mM, $[Ru(acac)_3]$ = 2 mM, T = 25 ºC

Hydrogen generation from the hydrolysis of sodium borohydride catalyzed by $Ru(acac)_3$ is compared to the self hydrolysis of sodium borohydride in Figure 3.2. It is seen clearly that the $Ru(acac)_3$ catalyst causes a significant increase in the rate of hydrogen generation from the hydrolysis of sodium borohydride.

In order to determine whether $Ru(acac)_3$ is homogeneous or heterogeneous catalyst, some poisoning experiments have also been performed.[37] One of the poisons used for this purpose was trimethylphosphite. Figure 3.3 shows the results of nine independent experiments, plotted as the relative rate of hydrogen generation versus the molar ratio of $P(OCH_3)_3/Ru(acac)_3$, which states that 1 equivalent $P(OCH_3)_3$ per ruthenium is sufficient to poison the $Ru(acac)_3$ catalyst. This is a convincing evidence for $Ru(acac)_3$ to be a homogeneous catalyst.

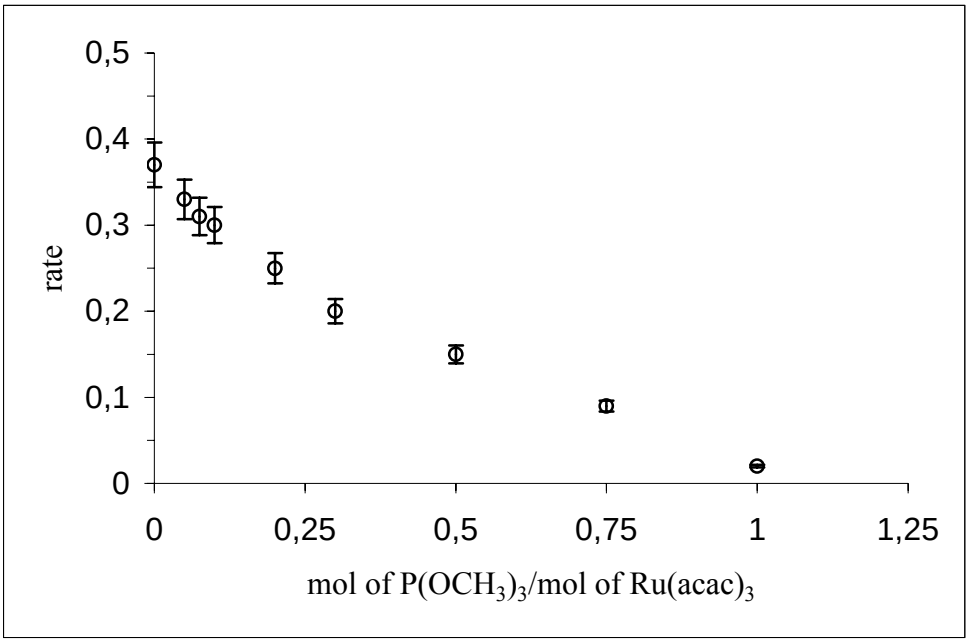

Figure 3.3 Plot of the relative rate versus the moles of $P(OCH_3)_3$/the moles of $Ru(acac)_3$ for the hydrolysis of sodium borohydride[37].

3.3. Catalytic Activity of Trimethylphosphite in the Hydrolysis of Sodium Borohydride

Although the addition of one equivalent $P(OCH_3)_3$ per ruthenium inhibits the catalytic activity of $Ru(acac)_3$ in the hydrolysis of sodium borohydride, the observation of the reaction for a longer time shows a sudden increase in the hydrogen generation rate after a certain period of time (hereafter, induction period). Figure 3.4 illustrates this phenomena clearly in the case of 2 equivalent $P(OCH_3)_3$ per ruthenium. After addition of 2 equivalent $P(OCH_3)_3$ per ruthenium to the reaction solution containing 150 mM $NaBH_4$ and 2 mM $Ru(acac)_3$ in 50 mL H_2O-THF solution, the hydrogen generation rate was reduced to the level of self

hydrolysis. After 55 minutes, a sudden, huge increase in the hydrogen generation rate (1170 mol H_2/mol Ru·h) is observed (Fig 3.4)

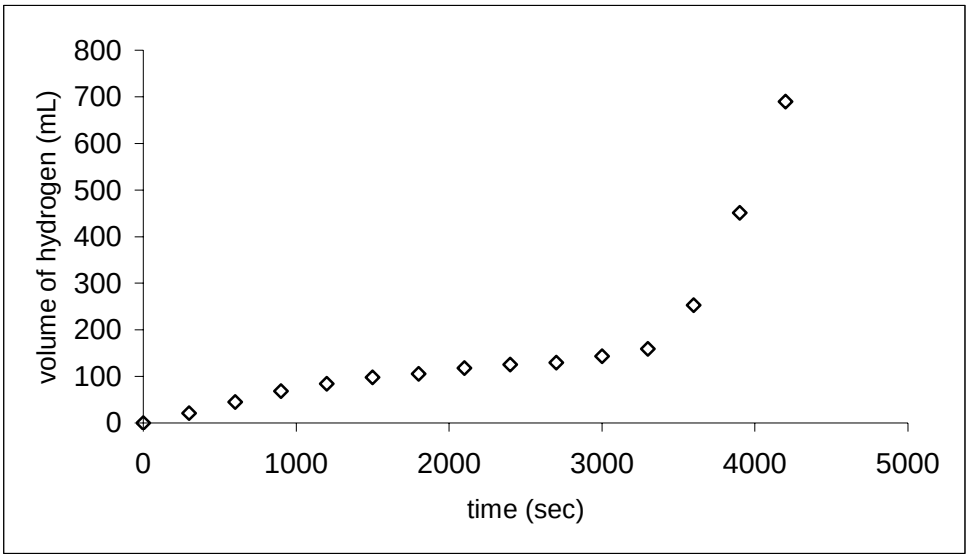

Figure 3.4 Plot of the volume of hydrogen generated versus time for the hydrolysis of sodium borohydride when [$NaBH_4$] = 150 mM, [$Ru(acac)_3$] = 2 mM, [$P(OMe)_3$]= 4 mM, T = 25 ºC

The next question to be addressed was which mole ratio of $P(OCH_3)_3$ / $Ru(acac)_3$ gives the highest catalytic activity in the hydrolysis of sodium borohydride. For that purpose, hydrolysis of sodium borohydride was catalyzed by $Ru(acac)_3$ and $P(OCH_3)_3$ system by changing molar ratio of $P(OCH_3)_3$ / $Ru(acac)_3$ as 1, 2, 3, and 4. Figure 3.5, 3.4, 3.6 and 3.7 show the catalytic activity of $Ru(acac)_3$ and $P(OCH_3)_3$ system at different molar ratios of $P(OCH_3)_3$ / $Ru(acac)_3$, respectively.

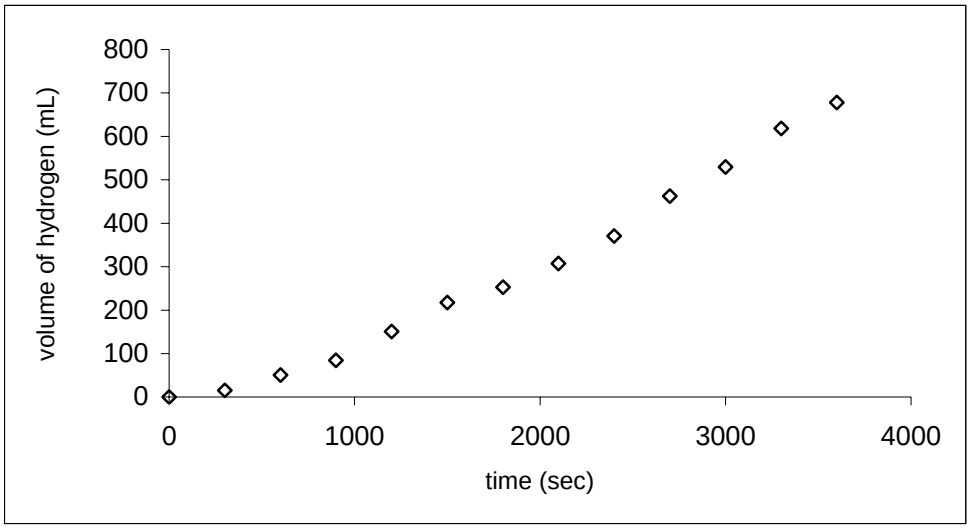

Figure 3.5 Plot of the volume of hydrogen generated versus time for the hydrolysis of sodium borohydride when [$NaBH_4$] = 150 mM, [$Ru(acac)_3$] = 2 mM, [$P(OMe)_3$]= 2 mM, T = 25 ºC

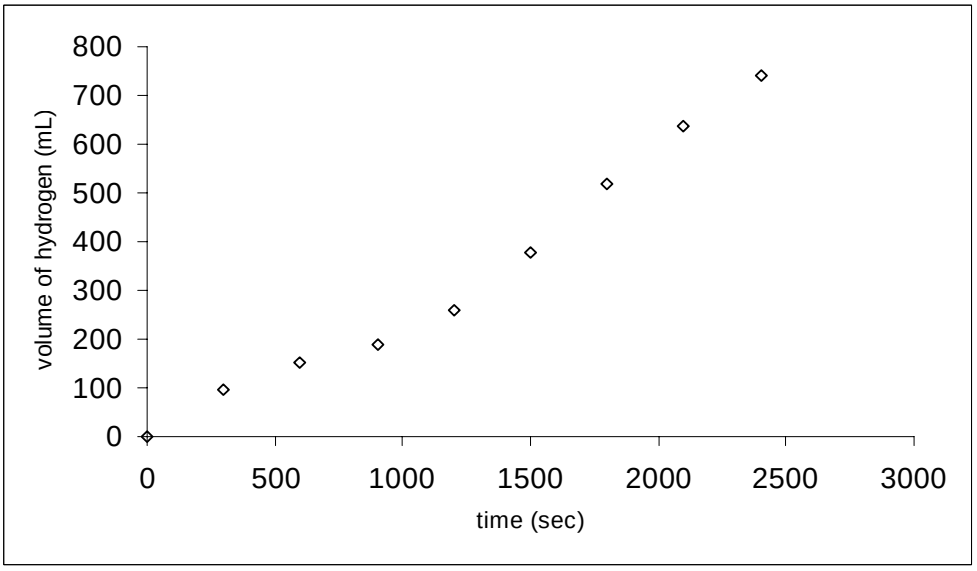

Figure 3.6 Plot of the volume of hydrogen generated versus time for the hydrolysis of sodium borohydride when [$NaBH_4$] = 150 mM, [$Ru(acac)_3$] = 2 mM, [$P(OMe)_3$]= 6 mM, T = 25 ºC

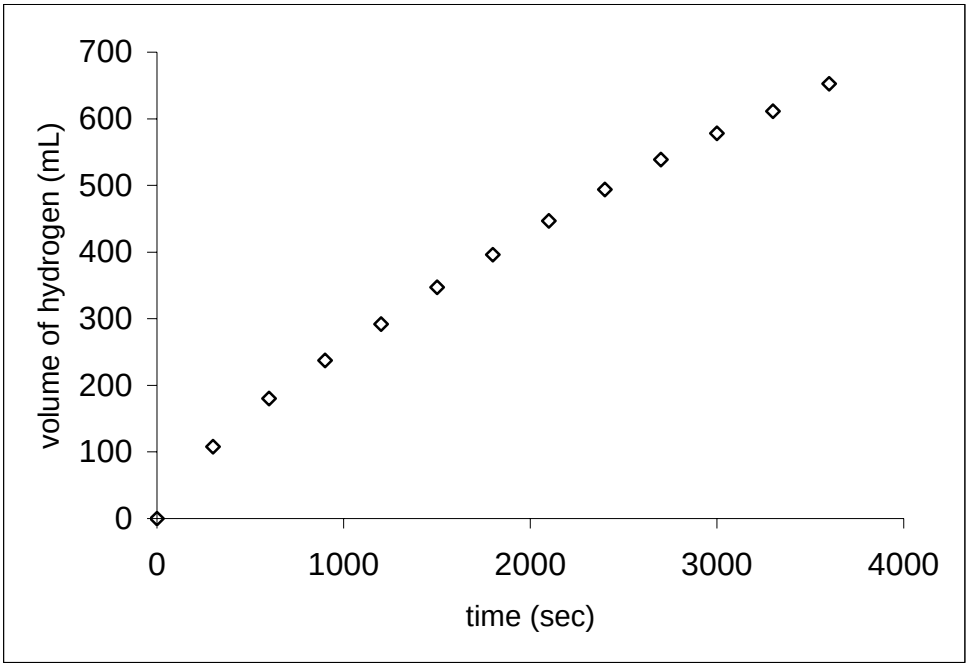

Figure 3.7 Plot of the volume of hydrogen generated versus time for the hydrolysis of sodium borohydride when [$NaBH_4$] = 150 mM, [$Ru(acac)_3$] = 2 mM, [$P(OMe)_3$]= 8 mM, T = 25 ºC

In order to decide on the highest activity of $Ru(acac)_3$ and $P(OCH_3)_3$ system, rate of hydrolysis of sodium borohydride was calculated for each mole ratio of $P(OCH_3)_3$ / $Ru(acac)_3$ and the results are listed in Table 3.1.

Table 3.1 Rate of hydrolysis of sodium borohydride for each mole ratio of $P(OCH_3)_3$ / $Ru(acac)_3$ starting with $[NaBH_4]$=150 mM, at 25 ºC

mole ratio of $P(OCH_3)_3$ / $Ru(acac)_3$	Rate of hydrolysis (mL H_2 / s)
1	0.246
2	**0.727**
3	0.421
4	0.146

The highest rate was observed when 2 equivalent $P(OCH_3)_3$ is used per ruthenium. In addition to rate, comparison of the induction period indicates that only when the mole ratio of $P(OCH_3)_3$ / $Ru(acac)_3$ is 2 an induction period is observed. In all the other cases the induction period is close to zero. The finding that the use of 2 equivalent $P(OCH_3)_3$ per ruthenium provides the highest catalytic activity implies that two phosphorous atoms may bind to ruthenium in the active complex giving the highest activity for hydrogen generation from the hydrolysis of sodium borohydride. Therefore, using a bidentate ligand may provide the highest activity for the hydrolysis of sodium borohydride when 1 equivalent bidentate ligand is used per ruthenium. For that purpose, we decided to use 1,2-bis(diphenylphosphino)ethane, dppe, together with $Ru(acac)_3$ as catalyst in the hydrolysis of sodium borohydride. However, the question, whether triphenylphosphine ligands would show an effect similar to trimethylphosphite in the hydrolysis of sodium borohydride catalyzed by ruthenium(III) acetylacetonate, needs to be answered before testing the dppe ligand in the same reaction. Therefore, triphenylphosphine, PPh_3, was used in the hydrolysis of sodium borohydride catalyzed by $Ru(acac)_3$ to see the effect of phenyl groups of the phosphine in the hydrolysis of sodium borohydride.

3.4. Catalytic Activity of The Ruthenium(III) acetylacetonate and Triphenylphosphine System

Since triphenylphoshine, PPh_3, is a monodentate ligand, 2 equivalents phosphorous per ruthenium were used. Catalytic hydrolysis of sodium borohydride (150 mM) starting with 2 mM $Ru(acac)_3$ and 4 mM PPh_3 system gives a result similar to that of the $Ru(acac)_3$ and $P(OCH_3)_3$ system. Figure 3.8 shows the catalytic activity of the $Ru(acac)_3$ and PPh_3 system in the hydrolysis of sodium borohydride. After an induction period of 30 minutes, a sudden, huge increase is observed in the rate of hydrolysis and a linear hydrogen generation starts with a rate of 970 mol H_2/mol Ru·h. This observation leads to the conclusion that the phenylphosphine ligands can also be used to enhance the catalytic activity of ruthenium(III) acetylacetonate in the hydrolysis of sodium borohydride.

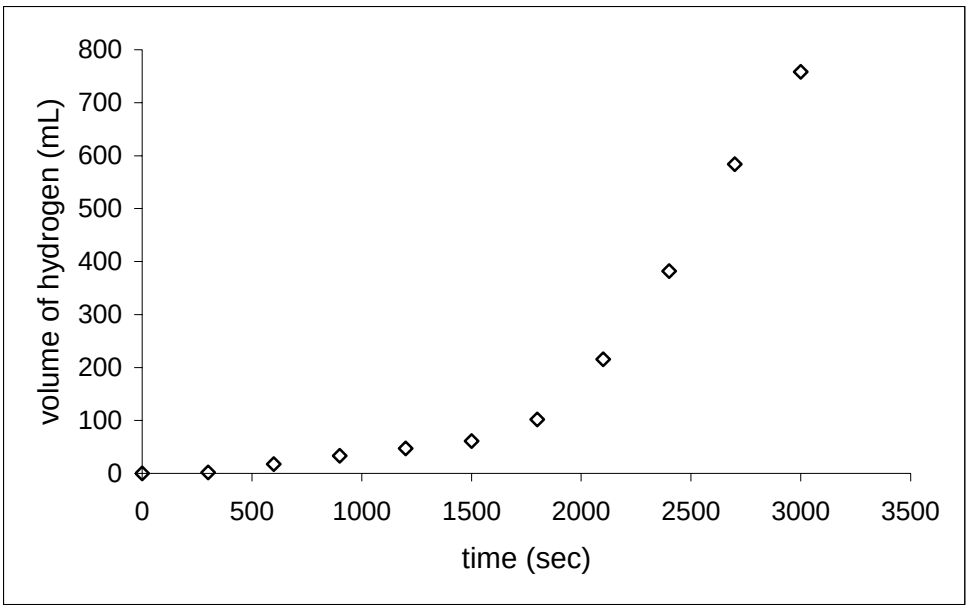

Figure 3.8 Plot of the volume of hydrogen generated versus time for the hydrolysis of sodium borohydride when $[NaBH_4]$ = 150 mM, $[Ru(acac)_3]$ = 2 mM, $[PPh_3]$= 4 mM, T = 25 ºC

3.5. Ruthenium(III) Acetylacetonate and 1,2-bis(dipheynylphosphino)ethane System: A Homogeneous Catalyst in the Hydrolysis of Sodium Borohydride

A recent study has shown that the phosphines act as poison on the homogeneous ruthenium(III) acetylacetonate catalyst in the hydrolysis of sodium borohydride,[37] for example, $P(OCH_3)_3$ and PPh_3 do so. As expected the bidendate ligand, 1,2-bis(dipheynylphosphino)ethane, also poisons the $Ru(acac)_3$ catalyst when added into the reaction medium during the hydrolysis of sodium borohydride (the initial part of the plot in Figure 3.9). However, after an induction period of 40 minutes, one observes a sudden increase in the rate of hydrogen generation from the hydrolysis of sodium borohydride. Then, hydrogen generation continues linearly with a rate of 1180 mol H_2/mol Ru·h.

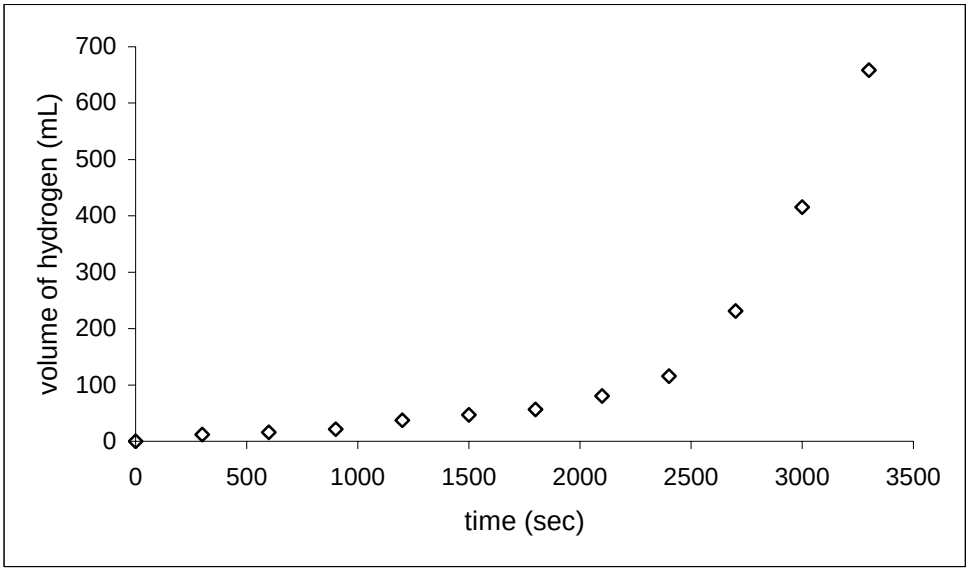

Figure 3.9 Plot of the volume of hydrogen generated versus time for the hydrolysis of sodium borohydride when $[NaBH_4]$ = 150 mM, $[Ru(acac)_3]$ = 2 mM, [dppe]= 2 mM, T = 25 ºC

The use of 1 equivalent 1,2-bis(dipheynylphosphino)ethane per ruthenium is based on the observation of the highest catalytic activity when two equivalent trimethylphosphite per ruthenium is used in the hydrolysis of sodium borohydride catalyzed by $Ru(acac)_3$ and $P(OCH_3)_3$ system. However, the validity of this finding that two equivalents of phosphines give the highest activity needs to be checked for dppe as well. In order to determine which mole ratio of dppe / $Ru(acac)_3$ gives the highest catalytic activity, a series of hydrolysis of sodium borohydride (150 mM) were performed starting with the various mole ratio of dppe/$Ru(acac)_3$ in the range of 0.5-2.5. Figure 3.10 shows the variation of the hydrogen generation rate with the dppe /$Ru(acac)_3$ mol ratio in the hydrolysis of sodium borohydride (150 mM) at 25 ºC.

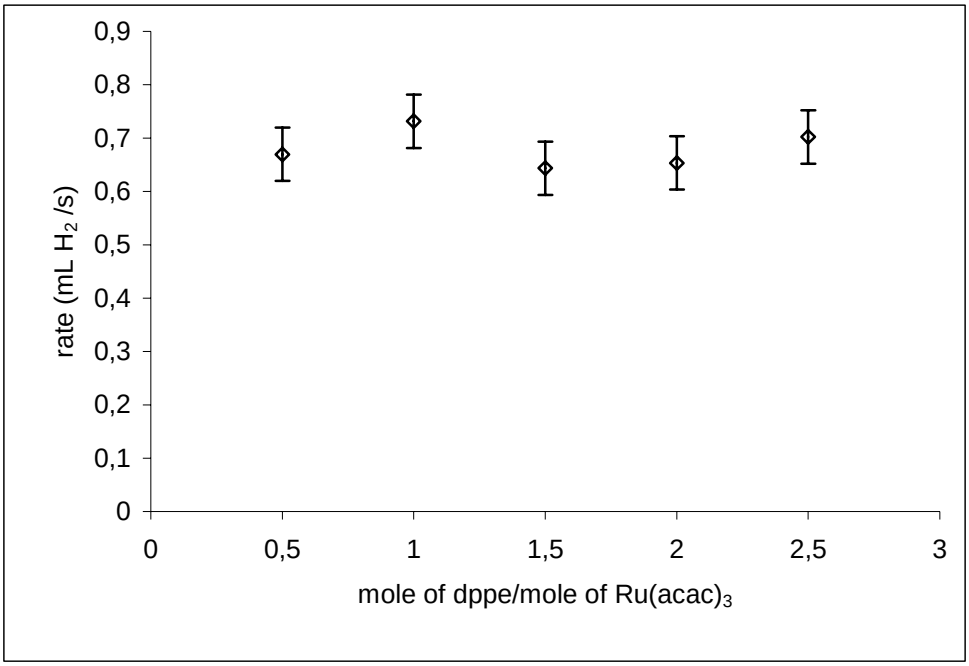

Figure 3.10 Plot of rate of hydrogen generation versus ratio of mole of dppe/mole of $Ru(acac)_3$ in the hydrolysis of sodium borohydride. $[NaBH_4]$ = 150 mM, T = 25 ºC.

The highest hydrogen generation rate appears when the dppe/$Ru(acac)_3$ mol ratio is 1, but the variation can be considered within the range of experimental error. Although the rate of hydrogen generation from the hydrolysis starts to increase slightly again after the dppe/$Ru(acac)_3$ mol ratio of 1.5, the risk of facing problems with the solubility of dppe at higher ratios make us to continue our study by keeping mole ratio of dppe/$Ru(acac)_3$ at 1.

3.6. Kinetic Study of the Hydrolysis of Sodium Borohydride Catalyzed by Ruthenium(III) Acetylacetonate Plus 1 Equivalent dppe

Kinetics of the hydrolysis of sodium borohydride catalyzed by ruthenium(III) acetylacetonate and 1 equivalent dppe were studied by monitoring the hydrogen evolution depending on substrate concentration, catalyst concentration and temperature.

$$NaBH_4 + 2\,H_2O \xrightarrow[\text{Water/THF (9:1)}]{Ru(acac)_3\ /\ dppe} NaBO_2 + 4\,H_2 \qquad (3.1)$$

3.6.1. The Rate Law for the Hydrolysis of Sodium Borohydride Catalyzed by Ruthenium(III) Acetylacetonate Plus 1 Equivalent dppe

Ruthenium(III) acetylacetonate and 1 equivalent 1,2-bis(diphenylphosphino)ethane was used for the first time as a homogeneous catalyst in the hydrolysis of sodium borohydride. Figure 3.11 shows the volume of H_2 versus time plots during the hydrolysis of sodium borohydride solution (450 mM) catalyzed by $Ru(acac)_3$ and 1 equivalent dppe in different ruthenium concentration at 25 °C.

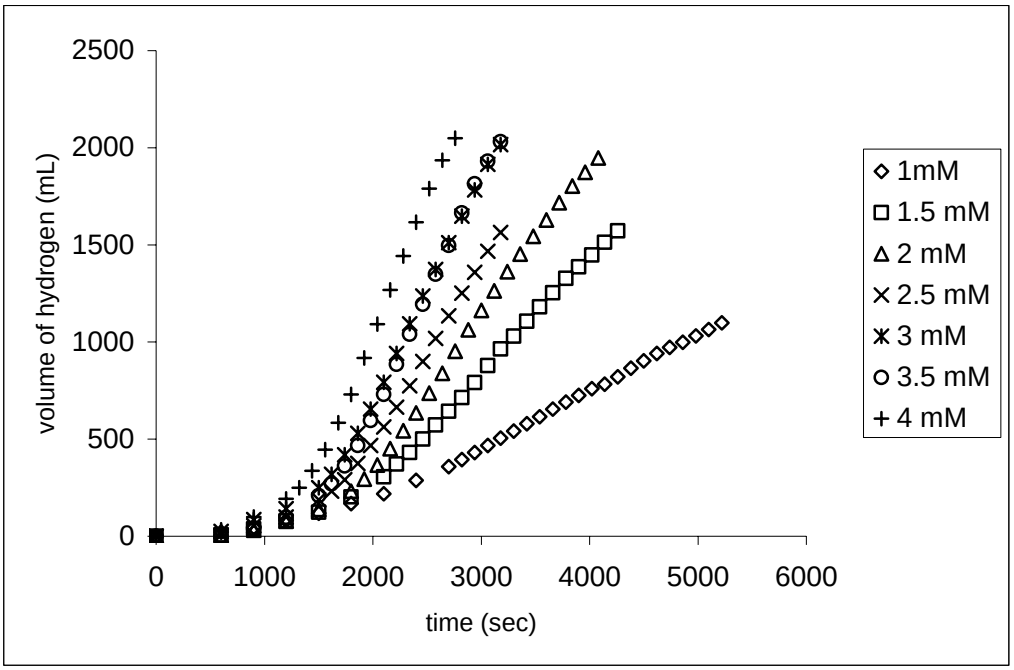

Figure 3.11 Volume of hydrogen generated versus time during $Ru(acac)_3$ and dppe system catalyzed hydrolysis of sodium borohydride with different catalyst concentrations by keeping $NaBH_4$ concentration constant at 450 mM and the dppe/ $Ru(acac)_3$ ratio at 1, at 25 °C .

Rate of hydrolysis of sodium borohydride catalyzed by $Ru(acac)_3$ and 1 equivalent dppe increases as the ruthenium concentration increases at 25 °C. However, induction period decreases with the increasing ruthenium concentration which is shown in Figure 3.12.

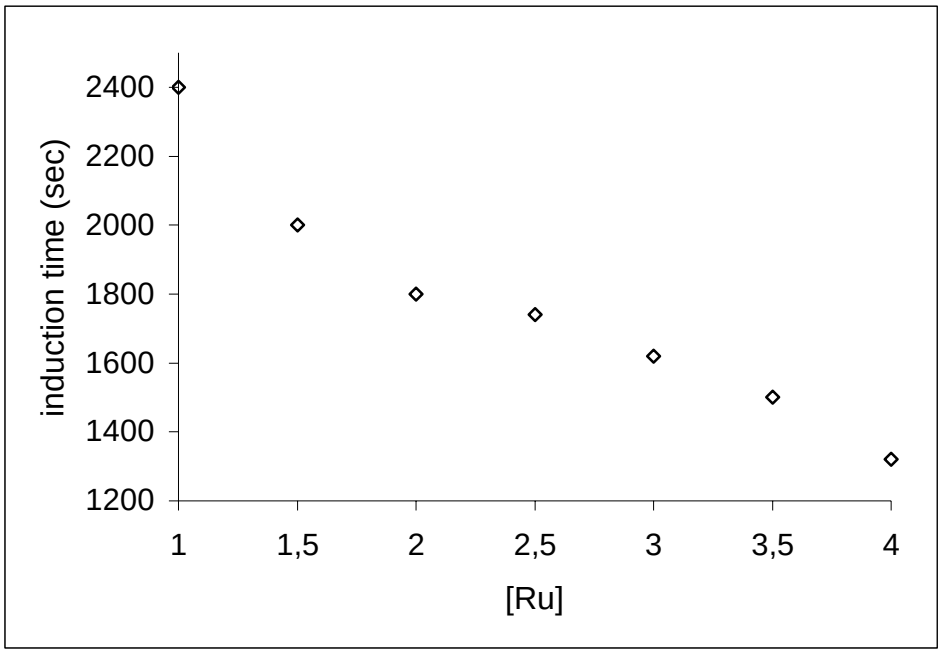

Figure 3.12 Induction time of hydrogen generation in the hydrolysis of sodium borohyride versus ruthenium concentration when 1 equivalent dppe is used for ruthenium by keeping $NaBH_4$ concentration constant at 450 mM at 25 °C .

It was observed that $Ru(acac)_3$ and 1 equivalent dppe catalyze the hydrolysis of $NaBH_4$ after an induction period of about 30-40 minutes even at low concentrations and room temperature.

In order to see rates of hydrogen generation from the hydrolysis of sodium borohydride catalyzed by $Ru(acac)_3$ and 1 equivalent dppe at different ruthenium concentrations, linear parts of the hydrogen generation plots for all the ruthenium concentrations are shown in Figure 3.13.

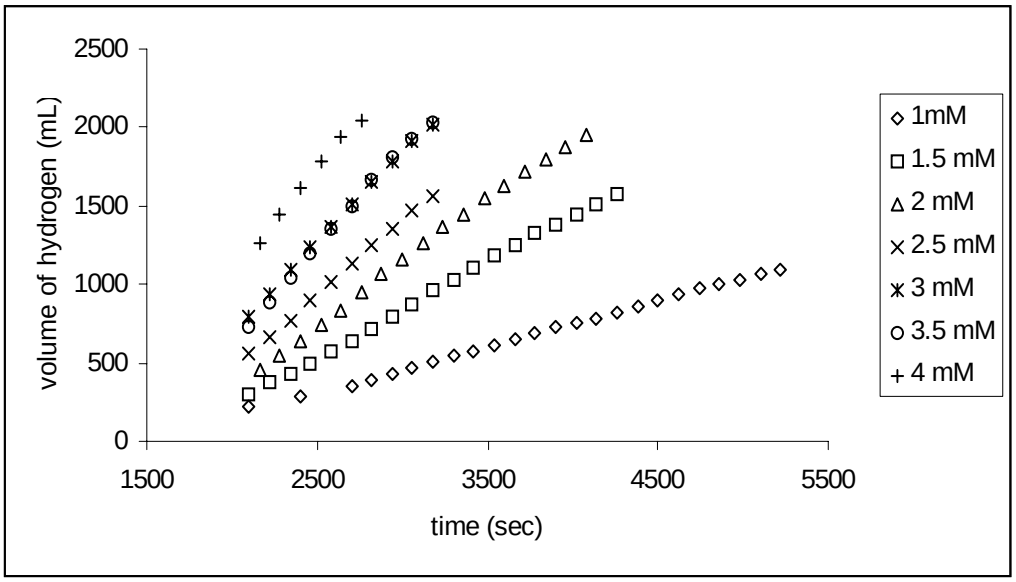

Figure 3.13 Linear parts of volume of hydrogen generated versus time plots during $Ru(acac)_3$ and dppe system catalyzed hydrolysis of sodium borohydride with different catalyst concentrations by keeping $NaBH_4$ concentration constant at 450 mM and the dppe/ $Ru(acac)_3$ ratio at 1, at 25 °C.

The hydrogen generation rate was determined from the linear portion of the plot for each experiment with $Ru(acac)_3$ / dppe system. Figure 3.14 shows the plot of hydrogen generation rate versus ruthenium concentrations, both in logarithmic scale.

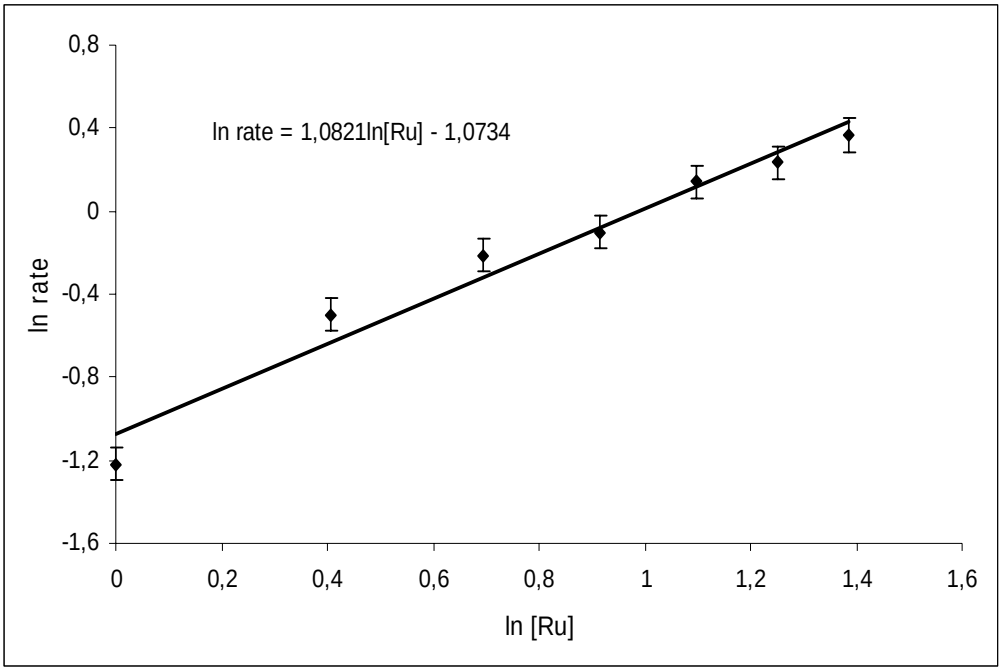

Figure 3.14 The graph of ln (rate) versus ln [Ru] for hydrolysis of sodium borohydride catalyzed by $Ru(acac)_3$ and 1 equivalent dppe at 25°C.

A straight line was obtained with a slope of about 1.0. This indicates that hydrolysis of sodium borohydride is first order with respect to the concentration of $Ru(acac)_3$ and dppe system.

Secondly sodium borohydride concentration was varied in the hydrolysis of $NaBH_4$ catalyzed by $Ru(acac)_3$ and 1 equivalent dppe by keeping ruthenium concentration constant at either 2 mM or 3 mM at 25.0 °C. Figure 3.15 shows the volume of hydrogen generated versus time when Ru concentration was kept at 2 mM and $NaBH_4$ concentration was varied in the range of 300, 600, 900, 1200 and 1500 mM.

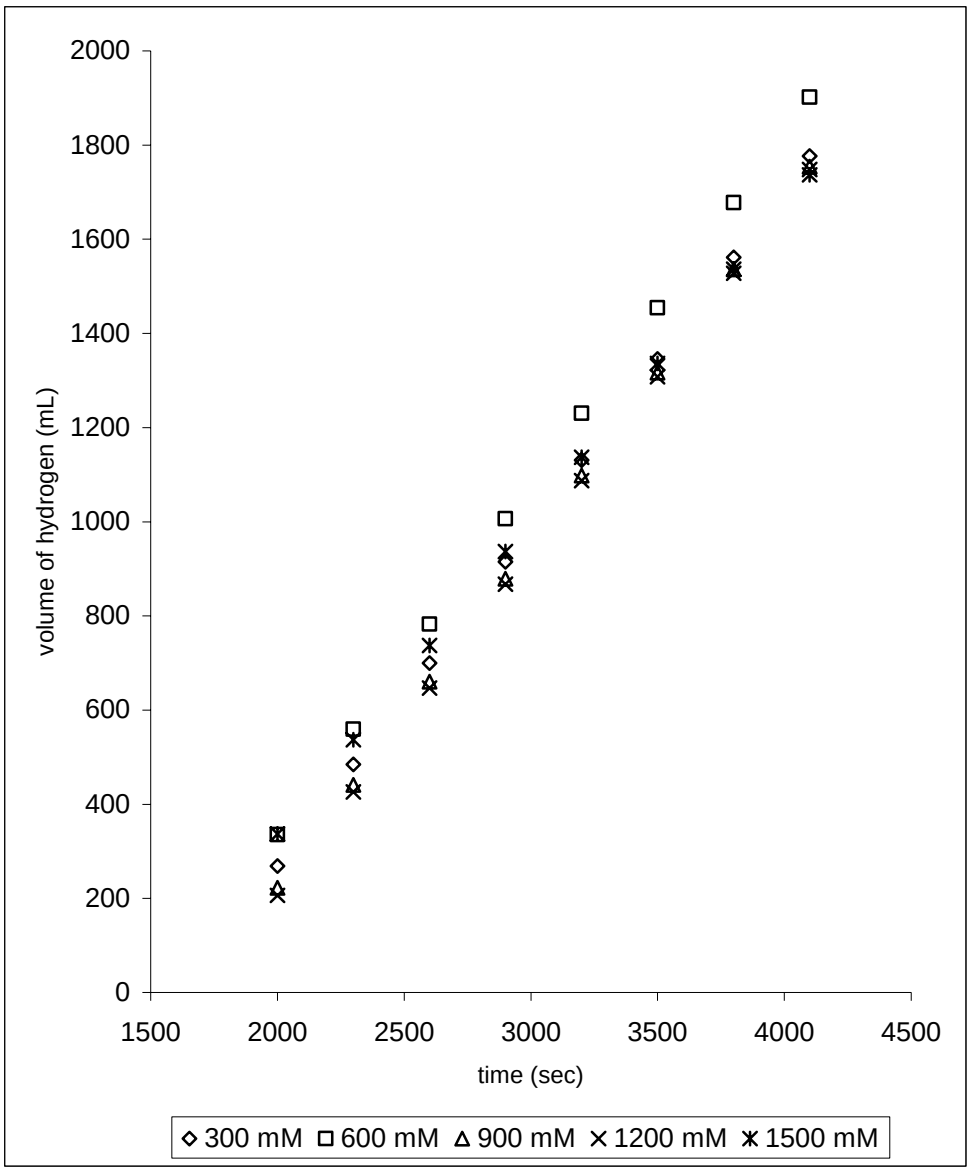

Figure 3.15 Volume of hydrogen generated versus time in the hydrolysis of sodium borohydride catalyzed by $Ru(acac)_3$ and 1 equivalent dppe by keeping ruthenium concentration at 2 mM and varying $NaBH_4$ concentration at 25.0 °C .

A straight line in logarithmic scale, shown in figure 3.16, gives a slope of -0.029 which indicates that rate of hydrolysis of sodium borohydride catalyzed by $Ru(acac)_3$ and 1 equivalent dppe is zero order with respect to $NaBH_4$ concentration.

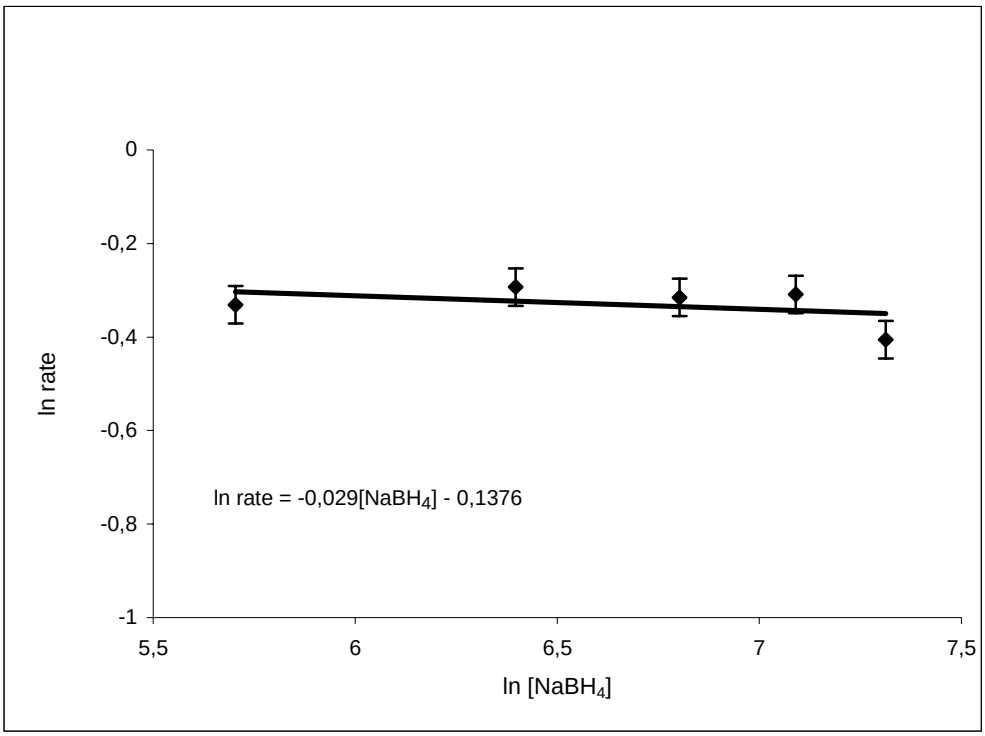

Figure 3.16 The graph of ln (rate) versus ln $[NaBH_4]$ for hydrolysis of sodium borohydride catalyzed by $Ru(acac)_3$ and 1 equivalent dppe when ruthenium concentration is kept constant at 2 mM at 25.0 °C.

The same study was repeated by keeping ruthenium concentration constant at 3 mM (dppe/ $Ru(acac)_3$ =1) and varying substrate concentration in the range of 300, 600, 900, 1200 and 1500 mM. Figure 3.17 shows the change in rate of hydrolysis of sodium borohydride when catalyst concentration is kept constant and substrate concentration is varied.

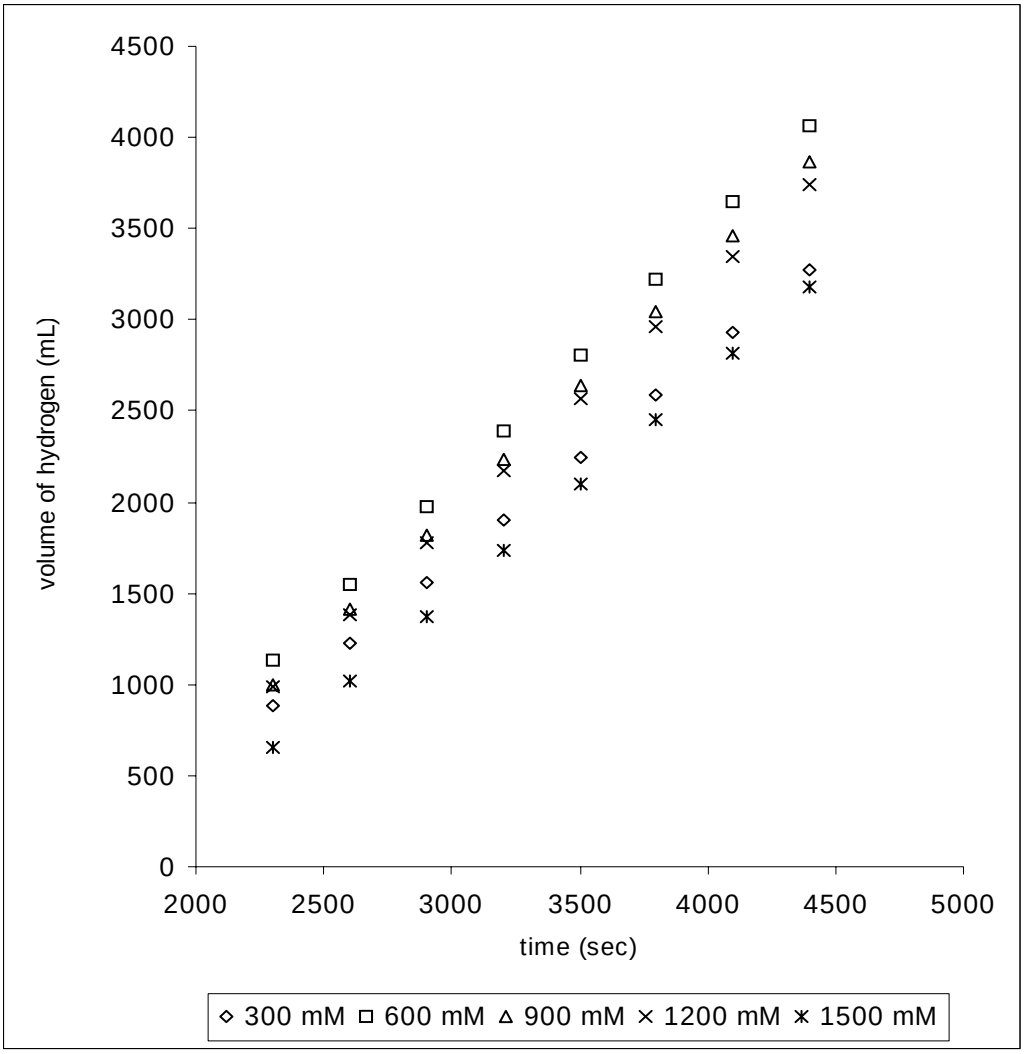

Figure 3.17 Volume of hydrogen generated versus time for the hydrolysis of sodium borohydride catalyzed by $Ru(acac)_3$ and 1 equivalent dppe, keeping ruthenium concentration constant at 3 mM and varying $NaBH_4$ concentration at 25.0 °C.

Similar result was obtained from the ln(rate) versus ln[$NaBH_4$] plot shown in Figure 3.18. The slope of the line is 0.0429 indicating that rate of hydrolysis is zero order with respect to $NaBH_4$ concentration.

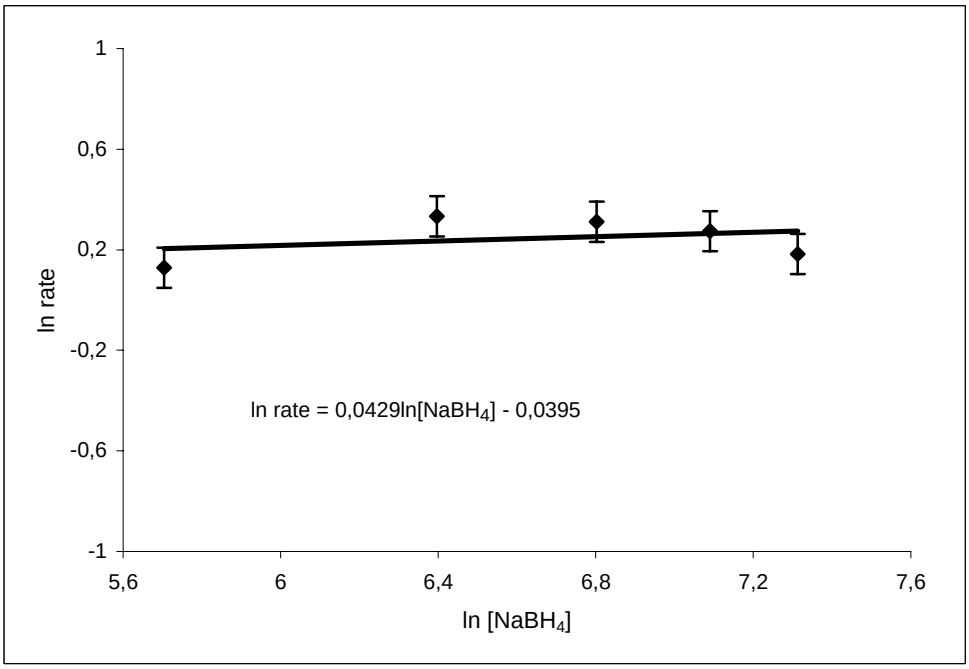

Figure 3.18 The graph of ln (rate) versus ln [$NaBH_4$] for the hydrolysis of sodium borohydride catalyzed by $Ru(acac)_3$ and 1 equivalent dppe when catalyst ruthenium concentration is kept constant at 3 mM and substrate concentration is varied at 25.0 °C.

Thus the rate law for the catalytic hydrolysis of sodium borohydride can be given as:

$$\frac{-4d[NaBH_4]}{dt} = \frac{d[H_2]}{dt} = k[Ru] \tag{3.2}$$

3.6.2. Activation Parameters for the Hydrolysis of Sodium Borohydride Catalyzed by Ruthenium(III) Acetylacetonate plus 1 Equivalent dppe

In order to find the activation parameters, hydrolysis of sodium borohydride catalyzed by $Ru(acac)_3$ and 1 equivalent dppe was studied at five different temperatures, 20, 25, 30, 35, and 40 °C. The change in the volume of hydrogen generated by time as the temperature increases is shown in Figure 3.19.

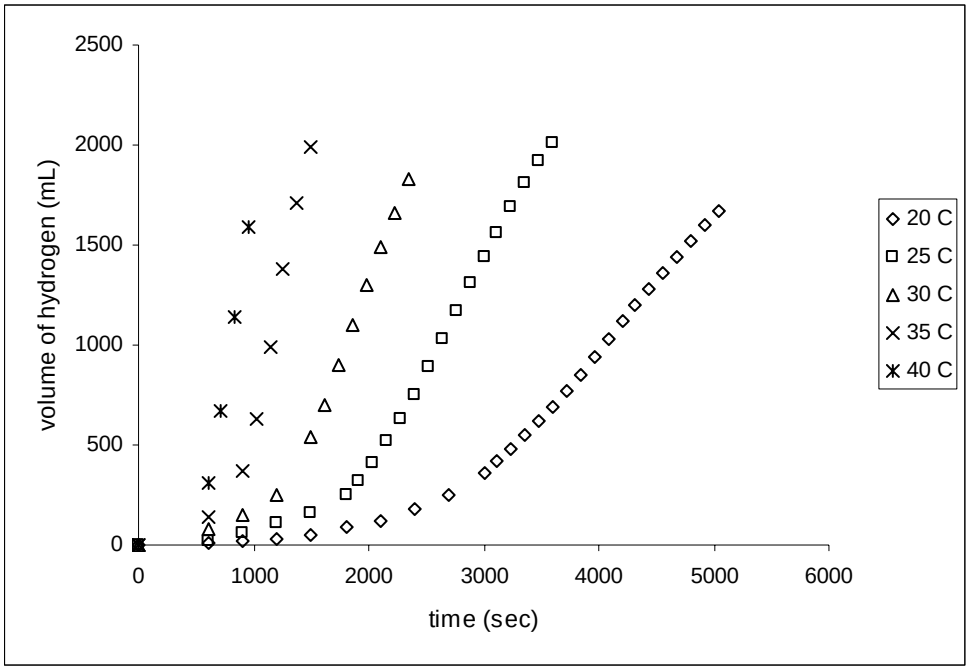

Figure 3.19 Plot of volume of hydrogen generated versus time for the hydrolysis of sodium borohydride catalyzed by $Ru(acac)_3$ and 1 equivalent dppe starting with a solution of 450 mM $NaBH_4$ and 2 mM ruthenium at different temperatures.

It was observed that rate of hydrolysis increases with the increasing temperature. However, induction period is inversely proportional with temperature; as the temperature increases, induction period is reduced.

Rate constants for $Ru(acac)_3$ and dppe system catalyzed hydrolysis of sodium borohydride at different temperatures are listed in Table 3.2.

Table 3.2 Rate constants for the hydrolysis of sodium borohydride catalyzed by $Ru(acac)_3$ and 1 equivalent dppe starting with a solution of 450 mM $NaBH_4$ and 2 mM ruthenium at different temperatures.

Temperature (°C)	**Rate Constant, *k*** **(mmol H_2). (mmol Ru)$^{-1}$· s^{-1}**
20	0.326 ± 0.0007
25	0.502 ± 0.008
30	0.722 ± 0.011
35	1.277 ± 0.044
40	1.604 ± 0.062

For the determination of the activation energy, the activation enthalpy and entropy, the rate constant / temperature data was evaluated using Arrhenius Equation :

$$k = A.e^{-\frac{Ea}{RT}} \tag{3.3}$$

where A is a characteristic constant, the preexponential factor, of the reaction, R is the gas constant and E_a is the Arrhenius activation energy. When the natural

logarithm of equation **1** is taken, the equation becomes:

$$\ell nk = \ell nA - \left(\frac{E_a}{RT}\right) \tag{3.4}$$

In Figure 3.20 the plot of ln k versus $\frac{1}{T}$ gives a straight line with a slope of $\left(-\frac{E_a}{R}\right)$ is shown:

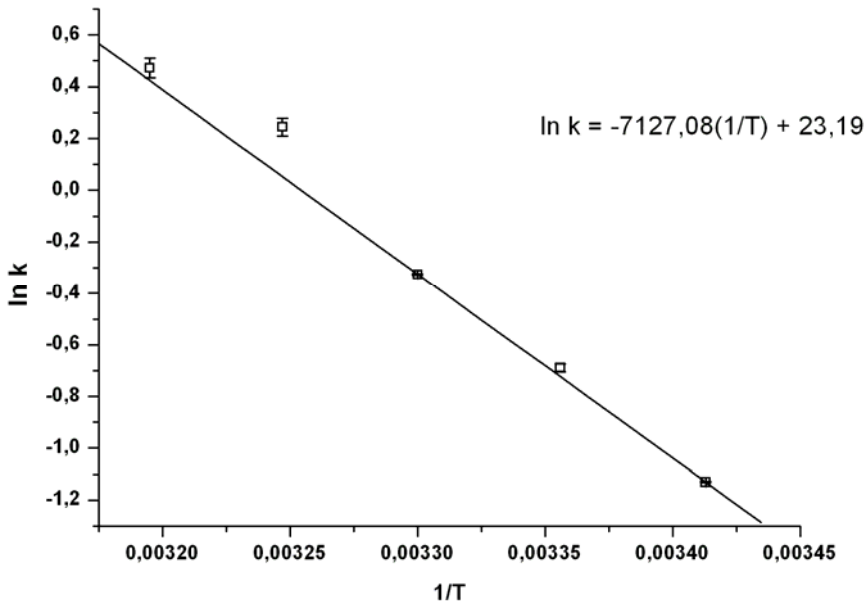

Figure 3.20 Arrhenius plot for the hydrolysis of sodium borohydride catalyzed by $Ru(acac)_3$ and 1 equivalent dppe at different temperatures. $[NaBH_4]$ = 450 mM and $[Ru(acac)_3]$ = 2 mM.

The activation energy, E_a, for $Ru(acac)_3$ and dppe system catalyzed hydrolysis of sodium borohydride was calculated to be 59 ± 2 kJ/mol using the slope of Arrhenius plot.

To calculate the enthalpy of activation, $\Delta H^{\neq}$ and the entropy of activation, $\Delta S^{\neq}$ Eyring equation **3** was used by drawing the plot of $\ln\frac{k}{T}$ versus $\frac{1}{T}$ which is shown in Figure 3.21.

$$\ln\frac{k}{T} = \frac{1}{T}\left(\frac{\Delta H^{*}}{R}\right) + \ln\frac{k_b}{h} + \frac{\Delta S^{*}}{R} \qquad (3.5)$$

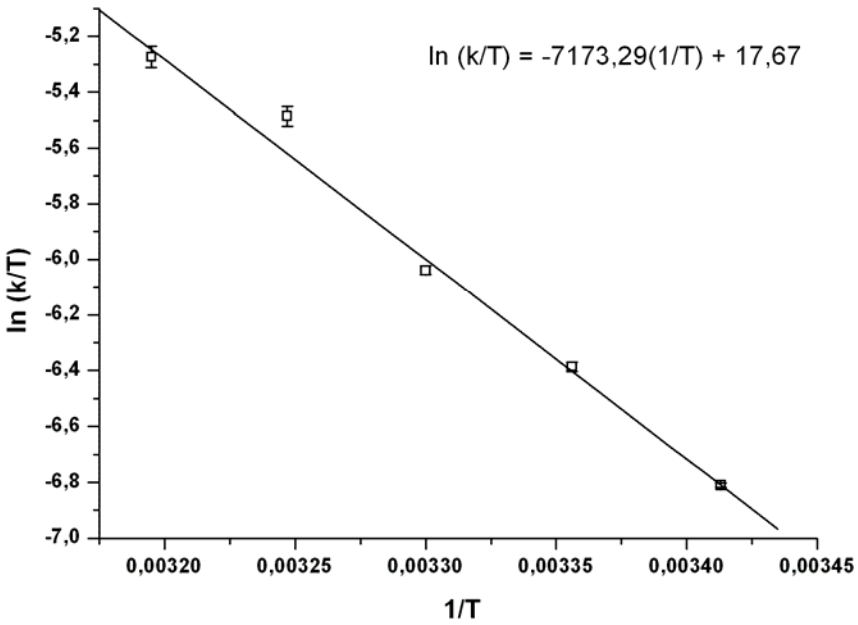

Figure 3.21 Eyring plot for the hydrolysis of sodium borohydride catalyzed by $Ru(acac)_3$ and 1 equivalent dppe. $[NaBH_4]$ = 450 mM and $[Ru(acac)_3]$ = 2 mM.

From the evaluation of the rate constant versus temperature data using the Eyring plot, the enthalpy of activation was calculated as 60 ± 1 $kJ.mol^{-1}$ and the entropy of activation was calculated as -50 ± 3 $J.(mol.K)^{-1}$ for the $Ru(acac)_3$ and dppe system catalyzed hydrolysis of sodium borohydride.

It is worth to compare these activation parameters to the values found for the hydrolysis of sodium borohydride catalyzed by ruthenium(III) acetylacetonate alone.[37] Both the activation energy (E_a = 59 ± 2 kJ/mol) and the enthalpy of activation ($\Delta H^{\neq}$ = 60 ± 1 $kJ.mol^{-1}$) found for the hydrolysis of sodium borohydride catalyzed by ruthenium(III) acetylacetonate and 1 equivalent dppe are slightly larger than the respective value for the same reaction catalyzed by ruthenium(III) acetylacetonate alone (E_a = 58.2 ± 2.6 $kJ.mol^{-1}$ and $\Delta H^{\neq}$ = 55.7 ± 2.5 $kJ.mol^{-1}$). The entropy of activation ($\Delta S^{\neq}$ = -50 ± 3 $J.(mol.K)^{-1}$) for the former reaction is smaller than that reported for the latter reaction ($\Delta S^{\neq}$ = 118 ± 5 $J{\cdot}mol^{-1}{\cdot}K^{-1}$).[37]

3.7. The Catalytic Life Time of Ruthenium(III) Acetylacetonate and 1 Equivalent dppe

The lifetime of catalyst is usually measured by the total turnover number of the catalyst for the given reaction. The total turnover number of $Ru(acac)_3$ and 1 equivalent dppe in the hydrolysis of sodium borohydride was determined to be 12250 turnovers over 1675 minutes in experiment starting with a 50 mL solution containing 2 mM ruthenium(III) acetylacetonate plus 2 mM dppe and 450 mM $NaBH_4$ at 25.0°C. Figure 3.22 shows the plot of total turnover number versus time for the hydrolysis of sodium borohydride catalyzed by $Ru(acac)_3$ and 1 equivalent dppe at 25.0 °C. The catalyst system comprising $Ru(acac)_3$ and 1 equivalent dppe provides 12250 turnovers over 1675 minutes in the hydrolysis of sodium borohydride at 25.0 °C. The turnover frequency was found to be 16 mol H_2 /mol Ru.min in the early stage of the hydrolysis.

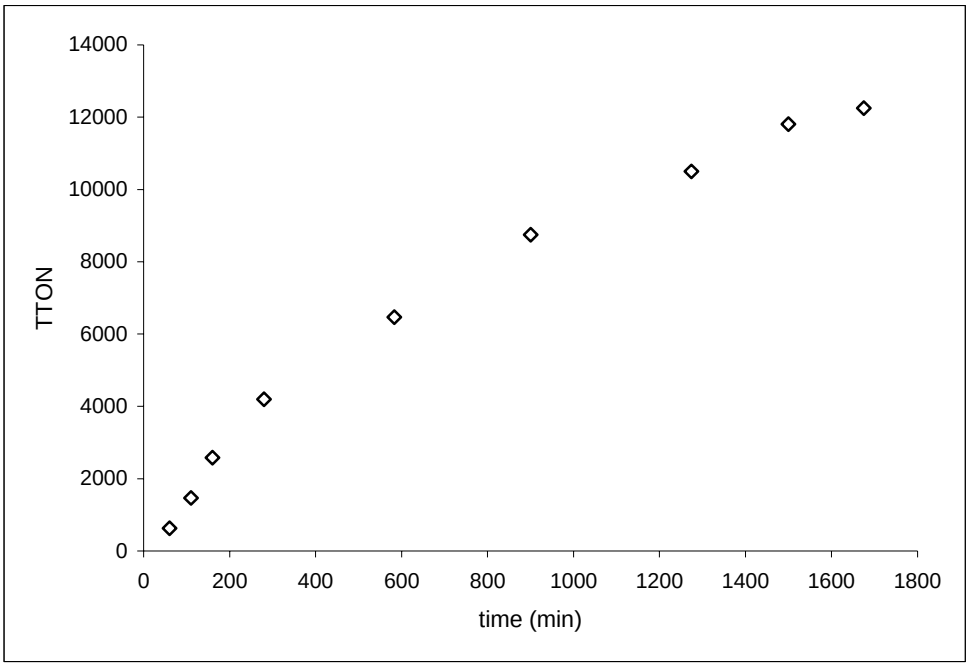

Figure 3.22 Plot of total turnover number versus time for the hydrolysis of sodium borohydride catalyzed by $Ru(acac)_3$ and 1 equivalent dppe, starting with a 50 mL solution containing 2 mM ruthenium and 450 mM $NaBH_4$ at 25.0°C.

3.8. Attempts to Identify the Active Catalyst

We tried to isolate active catalyst by crystallization but we obtained only the starting material, $Ru(acac)_3$ after the reaction. We can not say anything about the structure of the active catalyst.

3.8.1. UV-Visible Spectrum

Before following the hydrolysis of sodium borohydride reaction catalyzed by $Ru(acac)_3$ and 1 equivalent dppe, UV-visable spectra of $Ru(acac)_3$ with and without $NaBH_4$ were taken. Figure 3.23 shows the UV-visible electronic

absorption spectra of $Ru(acac)_3$ in the absence or presence of $NaBH_4$ added to the solution taken from the aqueous solution at 25 °C.

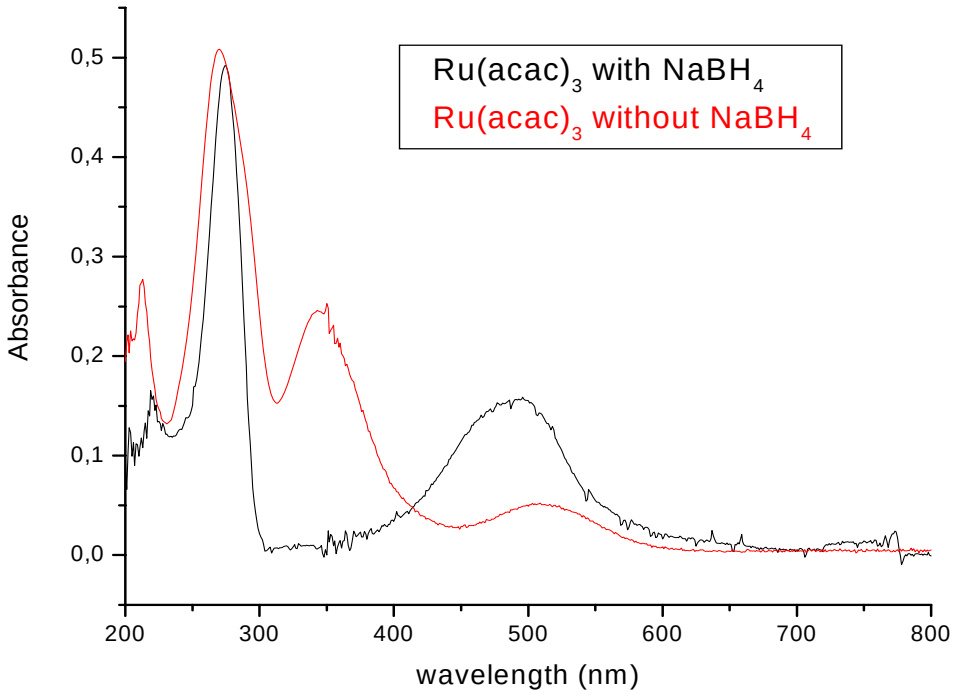

Figure 3.23 UV-visible spectra of $Ru(acac)_3$ in the presence (black) or absence (red) of 150 mM $NaBH_4$ in aqueous solution at 25 °C.

The spectrum of ruthenium(III) acetylacetonate shows three prominent absorption bands at 270, 350 and 509 nm. Upon addition of sodium borohydride into the solution, the band at 350 nm disappear while other two bands shift to higher energy, 275 and 496 nm, respectively.

It can be seen cleary that sodium borohydride causes significant changes in the absorption spectrum of $Ru(acac)_3$. Since the complex can be recovered with the same composition after catalytic reaction (after removing the sodium borohydride from the solution) this temporary change in the spectrum can be attributed to reduction of the ruthenium center. For comparison, the electronic absorption spectra of two similar octahedral complexes of ruthenium(II), $[Ru(en)_2IP]^{2+}$ **a**nd $[Ru(en)_2phen]^{2+}$, (IP: imidazo[4,5-*f*][1,10]phenanthroline and phen:1,10-phenanthroline) are shown in Figure 3.24 and 3.25, respectively.[40]

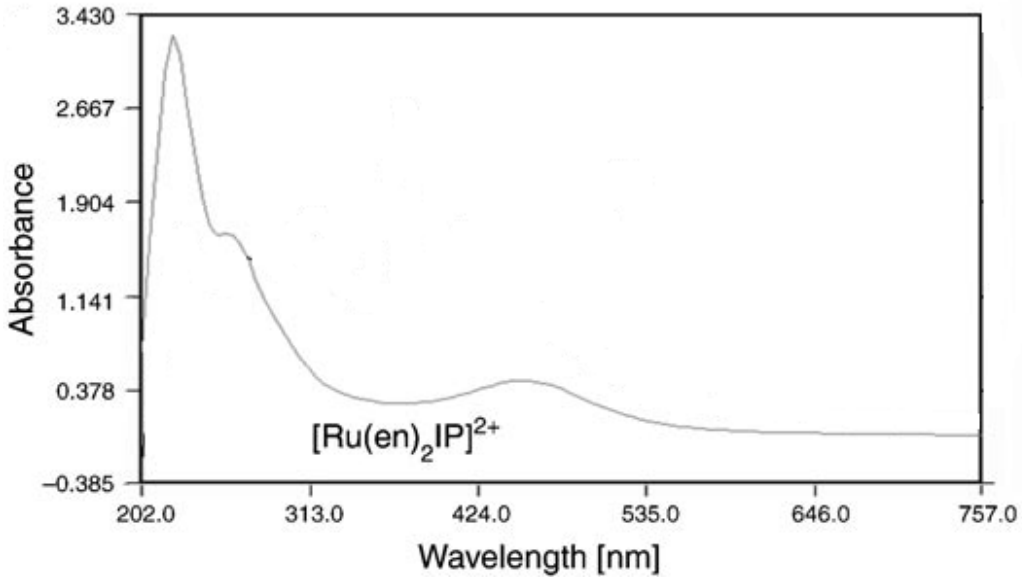

Figure 3.24 UV-vis spectrum of $[Ru(en)_2IP]^{2+}$ in aqueous solution at 25 °C [40].

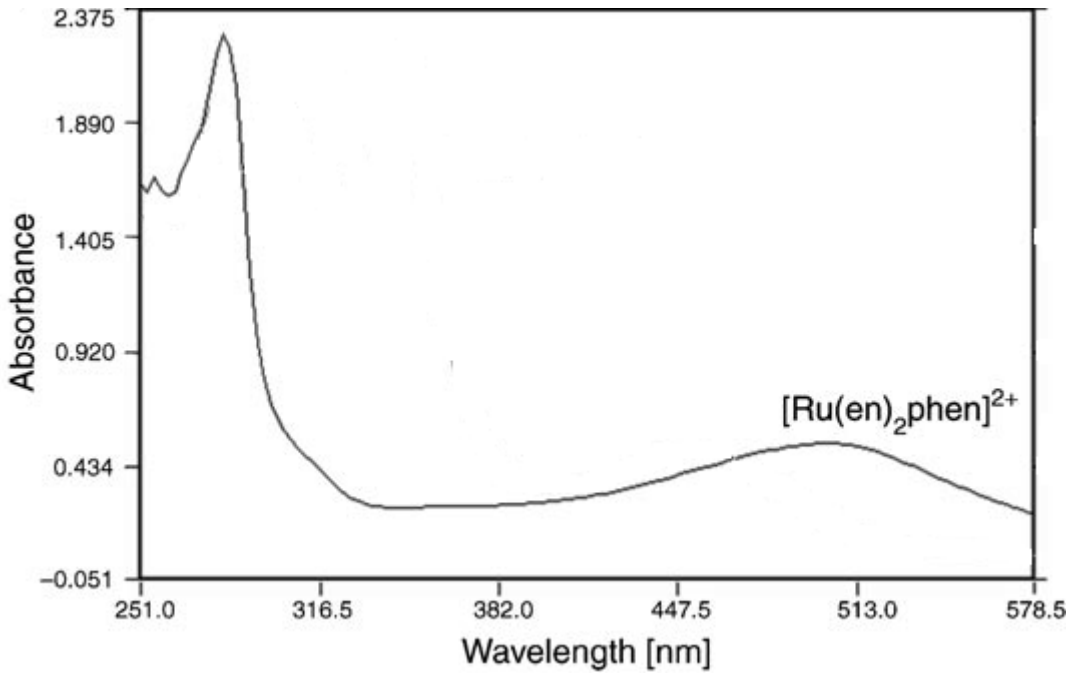

Figure 3.25 UV-vis spectrum of $[Ru(en)_2phen]^{2+}$ in aqueous solution at 25 °C [40].

These two Ru(II) complexes show absorption features similar to that of $Ru(acac)_3$ in the presence of $NaBH_4$ solution. From this comparison, it can be concluded that sodium borohydride reduces ruthenium(III) acetylacetonate to a ruthenium(II) species.

For a better appreciation of the change in the ruthenium complex, the electronic absorption spectra of the solution were taken for every ten minutes during the hydrolysis of sodium borohydride catalyzed by $Ru(acac)_3$ and 1 equivalent dppe at 25 °C. The results are shown in Figure 3.26 altogether.

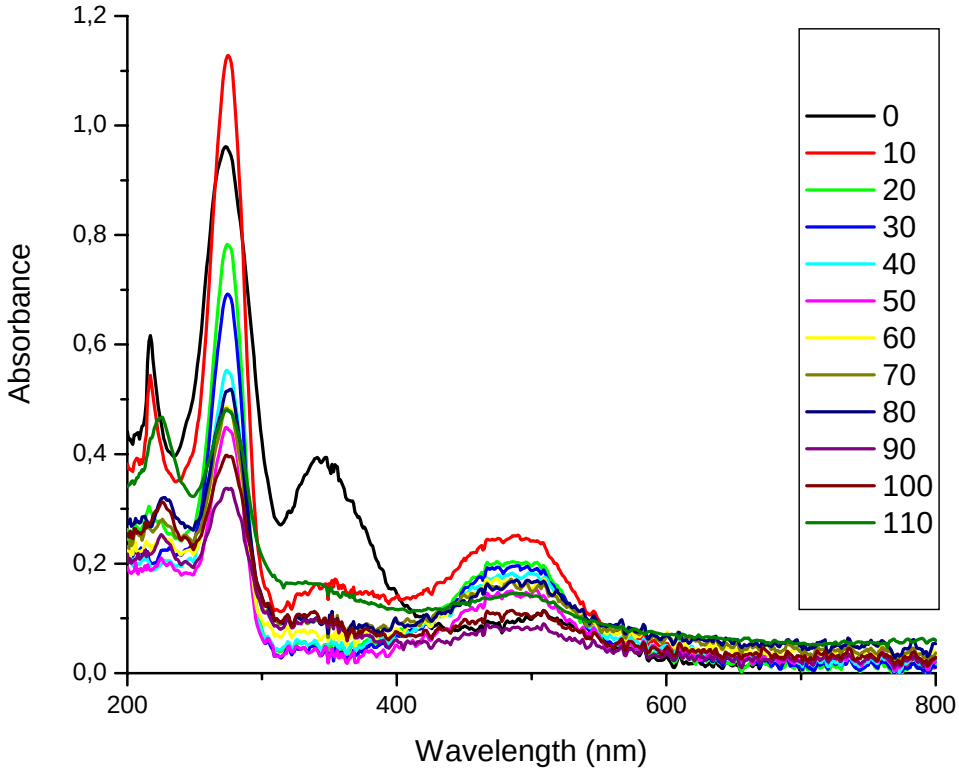

Figure 3.26 UV-Visible spectrum for the reaction of the hydrolysis of sodium borohydride catalyzed by $Ru(acac)_3$ and 1 equivalent dppe at different minutes.

It can be seen that $Ru(acac)_3$ is converted to a ruthenium(II) species during the hydrolysis (that is, in the presence of sodium borohydride). However, when all the sodium borohydride is hydrolyzed, the ruthenium(II) species is oxidized back to ruthenium(III). Interestingly, the electronic absorption spectra indicates that the ruthenium(III) acetylacetonate is generated back in the solution when all the sodium borohydride is hydrolyzed. Also, the only species we could isolate from the solution after hydrolysis is the ruthenium(III) acetylacetonate, without phosphine ligand.

One can conclude that ruthenium(III) is reduced to ruthenium(II) by sodium borohydride. A ruthenium(II) species involving phosphine ligand may be generated temporarily and acts as the active catalyst.

CHAPTER 5

CONCLUSIONS

In summary, our study on the $Ru(acac)_3$/dppe catalyzed hydrolysis of sodium borohydride have led to the following conclusions and insights:

(i) Ruthenium(III) acetylacetonate is a homogeneous catalyst in the hydrolysis of sodium borohydride.

(ii) As a phosphine ligand, 1,2-bis(diphenylphosphino)ethane (dppe) is expectedly a catalyst poison and inhibits the catalytic activity of $Ru(acac)_3$ when added to the hydrolysis solution, however, after an induction period a sudden and huge increase is observed in the rate of hydrolysis of sodium borohydride. In other words, the $Ru(acac)_3$/dppe system is acting as a homogeneous catalyst in the hydrolysis of sodium borohydride.

(iii) Ruthenium(III) ion is reduced to ruthenium(II) by sodium borohydride. A ruthenium(II) species involving the phosphine ligand may be generated in the solution and acting as active catalyst in the hydrolysis of sodium borohydride. However, the only species isolated from the solution after the catalytic reaction is the starting complex, ruthenium(III) acetylacetonate.

(iv) In the hydrolysis of $NaBH_4$ it is found that for $Ru(acac)_3$/dppe system is highly active catalyst providing 12250 total turnovers over 1675 minutes before they are deactivated. The turnover frequency was found to be 16 mol H_2 /mol Ru.min in the early stage of the reaction.

(v) The hydrolysis of sodium borohydride catalyzed by ruthenium(III) acetylacetonate and 1 equivalent dppe is first order in the catalyst concentration and zero order in the substrate concentration. Thus, the rate law for $Ru(acac)_3$ catalyzed hydrolysis of $NaBH_4$ is:

$$\frac{-4d[NaBH_4]}{dt} = \frac{d[H_2]}{dt} = k[Ru] \qquad (5.1)$$

(vi) The use of $Ru(acac)_3$/dppe system as catalyst provides the activation parameters comparable to those obtained ruthenium(III) acetylacetonate alone for the hydrolysis of sodium borohydride. The activation parameters are $E_a = 59 \pm 2$ kJ/mol), $A = 1.12 \times 10^{10}$ s^{-1}, $\Delta H^{\neq} = 60 \pm 1$ $kJ.mol^{-1}$ and $\Delta S^{\neq} = -50 \pm 3$ $J.(mol.K)^{-1}$.

(vii) That a phosphine ligand provides noticeable enhancement in the catalytic activity of ruthenium(III) acetylacetonate in the hydrolysis of sodium borohydride is an important piece of information which may be used in tailoring the homogeneous catalyst.

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