RUTHENIUM(III) ACETYLACETONATE; A HOMOGENEOUS CATALYST IN THE HYDROLYSIS OF SODIUM BOROHYDRIDE

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ABSTRACT

RUTHENIUM(III) ACETYLACETONATE; A HOMOGENEOUS CATALYST IN THE HYDROLYSIS OF SODIUM BOROHYDRIDE

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Ruthenium(III) acetylacetonate was employed for the first time as homogeneous catalyst in the hydrolysis of sodium borohydride. Ruthenium(III) acetylacetonate was not reduced by sodium borohydride under the experimental conditions and remains unchanged after the catalysis, as shown by FT-IR and UV-Vis spectroscopic characterization. Poisoning experiments with mercury, carbon disulfide or trimethylphosphite provide compelling evidence that ruthenium(III) acetylacetonate is indeed a homogenous catalyst in the hydrolysis of sodium borohydride.

Kinetics of the ruthenium(III) acetylacetonate catalyzed hydrolysis of sodium borohydride was studied depending on the catalyst concentration, substrate concentration and temperature. The hydrogen generation was found to be first order with respect to both the substrate concentration and catalyst concentration. The activation parameters of this reaction were also determined from the evaluation of the kinetic data: activation energy; $E_a = 25.6 \pm 1.3$ $kJ.mol^{-1}$, the enthalpy of activation; $\Delta H^{\#} = 24.6 \pm 1.2$ $kJ.mol^{-1}$ and the entropy of activation $\Delta S^{\#} = -170 \pm 5$ $J{\cdot}mol^{-1}{\cdot}K^{-1}$. Ruthenium(III) acetylacetonate provides the lowest activation energy ever found for the hydrolysis of sodium borohydride.

Ruthenium(III) acetylacetonate was found to be highly active catalyst providing 1183 total turnovers in the hydrolysis of sodium borohydride over 180 min before they are deactivated. The recorded turnover frequency (TOF) is 6.55 min^{-1}.

Keywords: Ruthenium(III) acetylacetonate, homogeneous catalyst, poisoning experiments, hydrolysis, sodium borohydride

ÖZ

RUTENYUM(III) ASETİLASETONAT; SODYUM BORHİDRÜRÜN HİDROLİZİNDE HOMOJEN KATALİZÖR

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Rutenyum(III) asetilasetonat, sodyum borhidrürün hidrolizinde ilk kez homojen katalizör olarak kullanıldı. Rutenyum(III) asetilasetonatın deney koşulları altında sodyum borhidrürle indirgenmediği ve katalitik tepkimeden sonra değişmeden kaldığı FT-IR ve UV-görünür bölge elektronik soğurma spektroskopisi yöntemleriyle belirlendi. Cıva, karbon disülfür ve trimetilfosfitle yapılan zehirleme deneyleri, rutenyum(III) asetilasetonatın sodyum borhidrürün hidrolizinde homojen bir katalizör olduğunu açıkça gösterdi.

Rutenyum(III) asetilasetonat tarafından katalizlenen sodyum borhidrürün hidroliz tepkimesinin kinetiği katalizör derişimine, sodyum borhidrür derişimine ve sıcaklığa bağlı olarak incelendi. Tepkime için geçerli olan aktivasyon parametreleri kinetik sonuçların ışığında hesaplandı: aktivasyon enerjisi, $E_a = 25.6 \pm 1.3$ kJ.mol^{-1}, aktivasyon entalpisi; $\Delta H^{\#} = 24.6 \pm 1.2$ kJ.mol^{-1}, aktivasyon entropisi; $\Delta S^{\#} = -170 \pm 5$

J·mol^{-1}·K^{-1}. Rutenyum(III) asetilasetonatın sodyum borhidrürün hidrolizinde katalizör olarak kullanılmasıyla, şimdiye kadar bulunan en düşük aktivasyon enerjisini sağladı.

Rutenyum(III) asetilasetonatın, etkinliğini kaybetmeden 180 dakikada sağladığı 1183 toplam çevirim sayısıyla sodyum borhidrürün hidrolizinde fazlasıyla etkin bir katalizör olduğu belirlendi. Kaydedilen çevrim frekansı (TOF) ise 6.55 min^{-1} olarak bulundu.

Anahtar kelimeler: Rutenyum(III) asetilasetonat; homojen katalizör; zehirlenme deneyleri; sodyum borhidrürün hidrolizi

To My Family

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CHAPTER 1

INTRODUCTION

Today in our world, the most important global problem is the high consumption of fossil fuels. At the present time, a large portion of the world energy demand is met by the fossil fuels because of their availability and convenient use.[1] However, it is expected that the world fossil fuels production will soon peak and then begin to decrease. It is estimated that[1], the fossil fuel production world wide will continue to rise for the next 15 years, and then will start to decrease. In the meantime, global energy and fossil fuel consumptions are expected to increase dramatically in the next decades, because of rising standards of living and a growing population worldwide. As planet Earth consumed more and more fossil fuels, two important predicaments started to emerge: (1) the depletion of fossil fuels in a foreseeable future, and (2) the global environmental problems caused by the fossil fuels and their combustion products.

The increasing demands for “clean” energy sources have resulted in an increased attention to “hydrogen economy” as a long-term solution for a secure energy future. The hydrogen economy offers a compelling vision of an energy future for the world that is at once abundant, clean, flexible, and secure. The hydrogen economy spans three functional areas: production, storage, and use of hydrogen; each area has its special set of grand technical challenges.

Effective storage and delivery of hydrogen, produced from sort of sources and intended for different uses, are key elements of the hydrogen economy because flexible use of hydrogen as a carrier of energy requires a means to store excess product for later use, to transport stored hydrogen from the point of production to the point of use, and to charge and discharge hydrogen conveniently from the storage container according to need. Advanced hydrogen storage concepts include metal hydrides, complex hydrides, e.g., alanates, carbon adsorption and nanostructured materials, e.g., carbon nano-tube encapsulation.

Recently, as a new fueling concept, it can be suggested that the chemical hydrides ($NaBH_4$, KBH_4, LiH, NaH, etc.) act as new fuel source supplying hydrogen at normal temperature.[2] Chemical hydrides are very reactive toward hydrolysis in water, which results in releasing a large amount of hydrogen gas. Among these chemical hydrides, sodium borohydride ($NaBH_4$) is in the group of highest energy content, both weight basis and volume basis[3] shown in Figure 1.1. Also it is a safe and practical means of producing hydrogen, but it's sensitive to moisture in air.

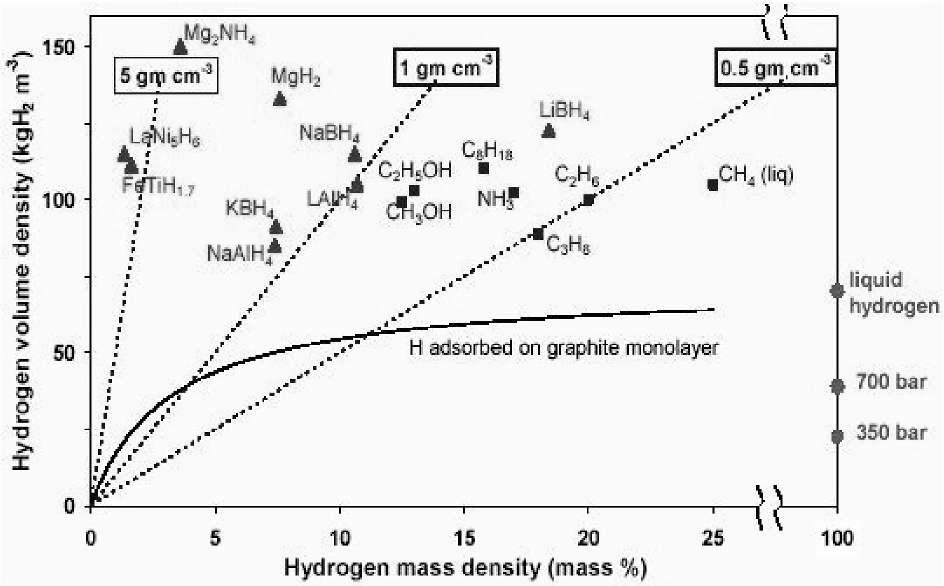


Figure 1.1 Volumetric hydrogen density versus gravimetric hydrogen density of various hydrogen containing compounds (taken from the literature[3]).

Hydrolysis of $NaBH_4$, produces hydrogen gas and water-soluble sodium metaborate, $NaBO_2$, in the presence of a suitable catalyst.[4] By this way, hydrogen can be generated safely for the fuel cells.

$$NaBH_4 + 2H_2O \xrightarrow{\text{catalyst}} NaBO_2 + 4H_2 \qquad \textbf{(1)}$$

Generating H_2 catalytically from $NaBH_4$ solutions has many advantages: $NaBH_4$ solutions are nonflammable, reaction products are environmentally benign, rate of H_2 generation is easily controlled, the reaction product $NaBO_2$ can be recycled, H_2 can be generated even at low temperatures. Such a hydrolysis of sodium borohydride can be accelerated by catalysts,[5] by acid,[6] or under elevated temperature.[7] To generate H_2 at the point of use, this easily and air-storable solution containing dissolved $NaBH_4$ is simply allowed to contact a catalyst. One clear advantage of this method is that rapid H_2 generation can be achieved at ambient temperatures (and even down to 0 ^{0}C) without mechanical compression, addition of water, acid or heat. In addition, since stabilized $NaBH_4$ solutions without catalyst produce very little H_2, and H_2 is only generated as needed, safety concerns about onboard storage of free H_2 are reduced.

In aqueous medium

$$BH_4^- + 2H_2O \longrightarrow BO_2^- + 4H_2 \qquad \textbf{(2)}$$

In acidic medium

$$BH_4^- + H^+ + 3H_2O \longrightarrow H_3BO_3 + 4H_2 \qquad \textbf{(3)}$$

The only other product of reaction, sodium metaborate (in solutions with pH > 11 the predominant solution product is sodium tetrahydroxyborate $NaB(OH)_4$), is water soluble and environmentally innocuous. Since the hyrolysis of sodium borohydride is completely inorganic reaction and does not contain sulfur, it produces virtually no fuel poisons such as sulfur compounds, carbon monoxide, soot, or aromatics. Therefore this reaction is considerably safer, more efficient, and easily controllable than producing H_2 by other chemical methods.[8] The heat generated by the reaction (75 kJ/mole H_2) formed is considerably less than (typical > 125 kJ/mole H_2), produced by reacting other chemical hydrides with water.[9] This promises a safer more controllable reaction.

The literature in catalytic hydrolysis of sodium borohydride dates back to 1953 and includes contributions from Schlesinger (platinum or rhodium salts),[10] Pecsok,[11] L. Brown,[12] C. Brown (iron, ruthenium, palladium, osmium, iridium, and platinum salts),[13] Stockmayer,[14] Davis,[15,16] Mesmer,[17] Gardiner,[18] Sen (nickel, Raney nickel, and bulk cobalt),[19] Amendola (bulk ruthenium),[20] Kojima (mixed metal/metal oxides such as Pt-$LiCoO_2$),[21, 22, 23] Hanxi (nickel boride),[24] Lee,[25] Wu,[26, 27] Kim,[28] Yang[29](filamentary nickel-cobalt). All of these catalysts used in hydrolysis of sodium borohydride so far are bulk metals and they act as heterogeneous catalysts.[30] The limited surface area of the heterogeneous catalysts causes to a lower catalytic activity as the activity of catalyst is directly related to its surface area. Thus, the use of metal nanoparticles with large surface area provides a potential route to increase the surface area and, thus, the catalytic activity.[31]

A recent study has shown that the water dispersible acetate stabilized ruthenium nanoclusters are highly active catalyst in the hydrolysis of sodium borohydride. [32] The ruthenium(0) nanoclusters have been prepared from the reduction of $RuCl_3$ by sodium borohydride in the presence of acetate ion as stabilizer.[32] In addition to the acetate anion, there exists also chloride anion in the solution which can be involved in the stabilization of ruthenium(0) nanoclusters. It is of considerable interest to use a precursor complex having an anionic ligand which can be used as a stabilizer for the ruthenium(0) nanoclusters formed from the reduction of the precursor complex. Since ruthenium(III) acetate is not known, ruthenium(III) acetylacetonate appears to be a promising candidate as the

precursor which would provide free acetylacetonate as precursor for the formation of ruthenium(0) nanoclusters in aqueous solution. Despite of many affords, ruthenium(III) acetylacetonate could not be reduced by sodium borohydride. However, ruthenium(III) acetylacetonate was found to be an active catalyst already in its present form for the hydrolysis of sodium borohydride in aqueous solution. This accidental discovery prompted us to employ ruthenium(III) acetylacetonate as homogenous catalyst in the hydrolysis of sodium borohydride and investigate this catalytic reaction in detail.

This dissertation work aims to use a homogeneous catalyst, ruthenium(III) acetylacetonate ($Ru(acac)_3$) (Figure 1.2) for the hydrolysis of sodium borohydride to generate hydrogen gas even at low temperature. Besides this, this dissertation work shows that $Ru(acac)_3$ is not a suitable precursor in the synthesis of water-dispersible Ru(0) nanoclusters. It is novel as reporting for the first time the results of our study on the hydrogen generation from the catalytic hydrolysis of sodium borohydride using a homogeneous catalyst.

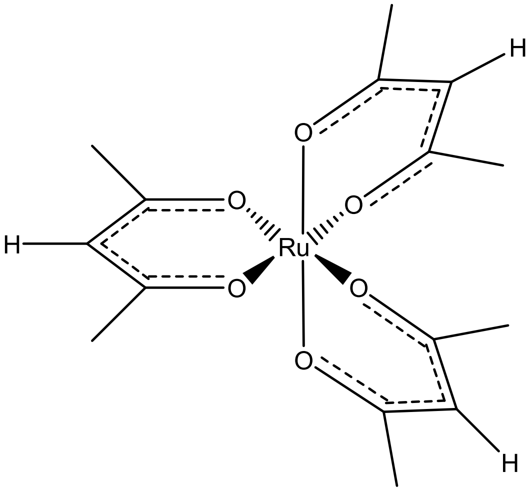


Figure 1.2 Ruthenium(III) acetylacetonate

CHAPTER 2

CATALYSTS

2.1. Introductory Concepts of Catalysts

A thermodynamically favorable reaction may be slow at modest temperatures and therefore not of value for synthesis. Increasing the temperature of the reaction may significantly accelerate its rate, but providing the energy to do so is expensive and higher temperatures may induce competing side reactions that will greatly reduce product yields. A more attractive approach to increasing the rate of reaction is to use a catalyst.[33]

A catalyst is a substance that increases the rate of a reaction but is not itself consumed. Catalysts are widely used in nature, in industry, and in the laboratory, and it is estimated that they contribute to one-sixth of the value of all manufactured goods in industrialized countries. For example, a key step in the production of a dominant industrial chemical, sulfuric acid, is the catalytic oxidation of SO_2 to SO_3. Ammonia, another chemical essential for industry and agriculture, is produced by the catalytic reduction of N_2 by H_2. Inorganic catalysts are also used for the production of the major organic chemicals and petroleum products, such as fuels, petrochemical, and polyalkene plastics. Catalysts play a steadily increasing role in achieving a cleaner environment, both through the destruction of pollutants and through the development of cleaner industrial processes with less abundant byproducts.

A catalyst increases the rates of process by introducing new pathways with lower Gibbs energies of activation $\Delta G^{\#}$. Figure 2.1. illustrates the energetics in a catalytic cycle. The uncatalyzed reaction has a higher Gibbs energy of activation than any step in the catalyzed reaction. The Gibbs energy of reaction $\Delta_r G^{\theta}$, for the overall reaction is unchanged from (a) to (b).[34]

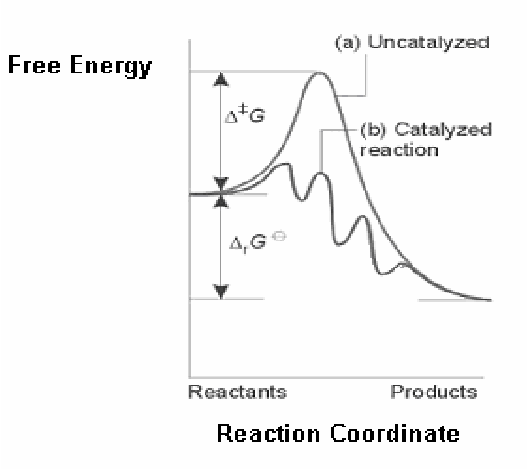


Figure 2.1 A schematic representation of the reaction profile of a reaction without and with catalyst (Adapted from the literature[34])

Catalysts are of enormous importance to the chemical industry, because they allow a reaction to occur with a reasonable rate at a much lower temperatures than otherwise; lower temperatures translate into lower energy costs. Moreover, catalysts are often quite specific-they increase the rate of certain reactions, but not others. For instance, an industrial chemist can start with a mixture of carbon monoxide and hydrogen and produce methane gas using one catalyst or produce gasoline using another catalyst. The most remarkable catalysts are enzymes.

Enzymes are the marvelously selective catalysts employed by biological organisms. A biological cell contains thousands of different enzymes that in effect direct all of the chemical processes that occur in the cell.[35]

The use of transition metal complexes for reductive catalysis is widespread. In general, the transition metal complex added to the reaction is not the true catalyst. Rather the added complex is a precursor, or precatalyst, from which the true catalyst forms in situ. [36]

Catalysts are classified as heterogeneous if they are present in a different phase from that of the reactants.[34] Historically, many catalysts have been heterogeneous in nature; that is, solid materials having catalytically active sites on their surface, with only the surface in contact with reactants.[37] Catalysts are classified as homogeneous if they are present in the same phase as the reagents; this normally means that they are present as solutes in a liquid reaction mixture.[34]

2.2. Catalytic Cycles

The essence of catalysis is a cycle of reactions that consumes the reactants, forms products and regenerates the catalytic species. A catalyzed reaction pathway is usually represented by a catalytic cycle. A catalytic cycle consists of a series of stoichiometric reactions (often reversible) that form a closed loop; the catalyst must be regenerated so that it can participate in the cycle of reactions more than once. For a catalytic cycle to be efficient, the intermediates must be short-lived. The downside of this for understanding mechanism is that short lifetimes make studying a cycle difficult. Experimental probes are used to investigate the kinetics of a catalytic process, isolate or trap the intermediates, attempt to monitor intermediates in the cycle.[34]

One of the most studied catalytic systems is the Wilkinson's catalyst. As an example for a catalytic cycle the hydrogenation of cyclohexane by Wilkinson's catalyst is shown in Figure 2.2:

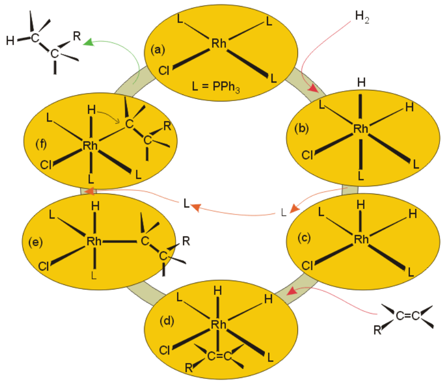


Figure 2.2 "Catalytic cycle" view of the Wilkinson catalyst (Adapted from the literature[34])

2.3. Properties of Catalysts

In the modern industrial economy, catalysis forms the cornerstone of the chemical and petroleum industries. Process throughputs are large, and therefore even minor improvements in catalyst performance can have a substantial economic return.[38] The usefulness of a catalyst depends principally on some factors such as activity, selectivity and life-time.

2.3.1. Catalytic Activity

In the speciation of catalytic activity, a number of measures is available to the experimenter which includes the following:

1. The reactant conversion or product yield achieved under given reaction conditions (e.g. temperature, pressure, reactant space velocity).

2. The reaction rate under given conditions.

3. The temperature necessary to obtain a given degree of conversion or yield.

4. The reactant space velocity necessary to achieve a given conversion or yield under specified reaction conditions.

5. Rate constants derived from a kinetic study of the system at a particular temperature.

The criterion chosen will be determined mainly by the purpose for which the information is required and the number of catalysts to be tested.[38] For this reason it is logical to define catalytic activity using the concept of turnover frequency or turn over number.[39]

2.3.1.1. Turnover Frequency and Turnover Number

The catalytic turnover number (TON) is the number of moles of product per mole of catalyst; this number indicates the number of catalytic cycles for a given process, e.g. after 2 hours the TON was 2400. The catalytic turnover frequency (TOF) is the catalytic turnover per unit time: the number of moles of product per mole of catalyst per unit time, e.g. the TOF was 20 min^{-1}.

If we consider the conversion of A to B catalyzed by Q and with a rate ν the catalytic turnover number and turnover frequencies can be given as follows.

$$A \xrightarrow{Q} B \quad v = \frac{d[B]}{dt} \tag{4}$$

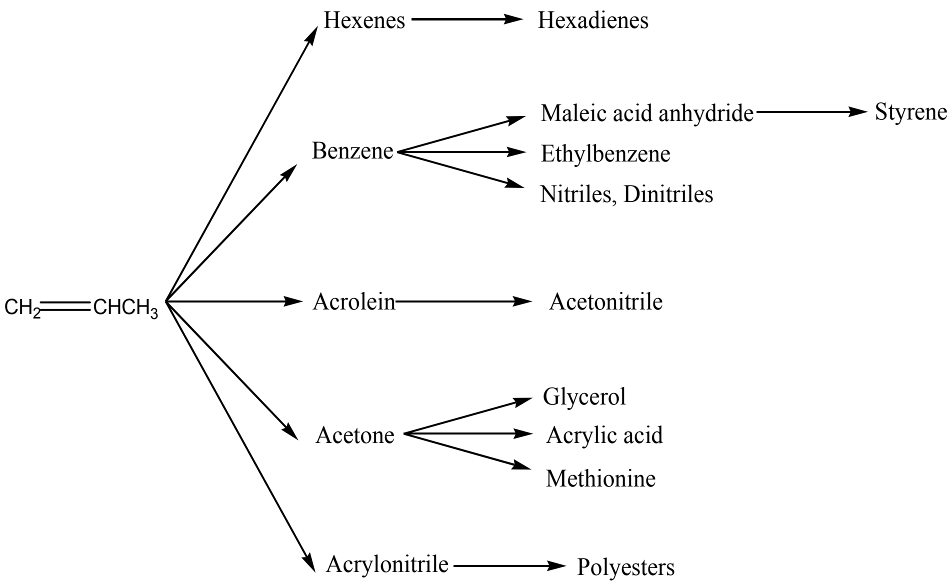
$$TON = \frac{[B]}{[Q]} = \frac{\text{moles of product}}{\text{moles of catalyst}} \tag{5}$$

$$TOF = \frac{v}{[Q]} = \frac{\text{moles of product}}{\text{moles of catalyst} \times \text{time}} \tag{6}$$

Defining the catalytic turnover number and frequency is not without problems. For example, if there is more than one product, one should distinguish between values of the total TON and TOF for all the catalytic products, and specific values for individual products. The term catalytic turnover number is usually used for batch processes, where as catalytic turnover frequency is usually applied to continuous process.[40]

2.3.2. Selectivity

A good catalyst must possess both high activity and long-term stability. But its single most important attribute is its selectivity, which reflects its ability to direct conversion of the reactant(s) along one specific pathway.[39]A selective catalyst yields a proportion of the desired product with minimum amounts of side products. In industry, there is considerable economic incentive to develop selective catalysts.[34] For example depending upon the solid catalyst employed, one or other of the products shown in Scheme 1 can be selectively generated from propylene.[39]



Scheme 1 The products of propylene depending upon the solid catalyst (Adapted from the literature[39])

For a specific catalyst the selectivity will be function of the reaction temperature, pressure, space velocity, composition of the feed, reactor geometry and degree of conversion. Therefore, a lot of experiments are have to be done in order to give a satisfactory description of the selectivity characteristics of a particular catalyst/reaction combination.[38]

2.3.3. Lifetime

Catalyst life may be defined by the time taken to reach a specified minimum activity.[38]A small amount of catalyst must survive through a large number of cycles if it is to be economically viable. However, a catalyst may be destroyed by side reactions to the main catalytic cycle or by the presence of small amounts of impurities in the starting materials. Some catalysts can be regenerated quite readily.[34]

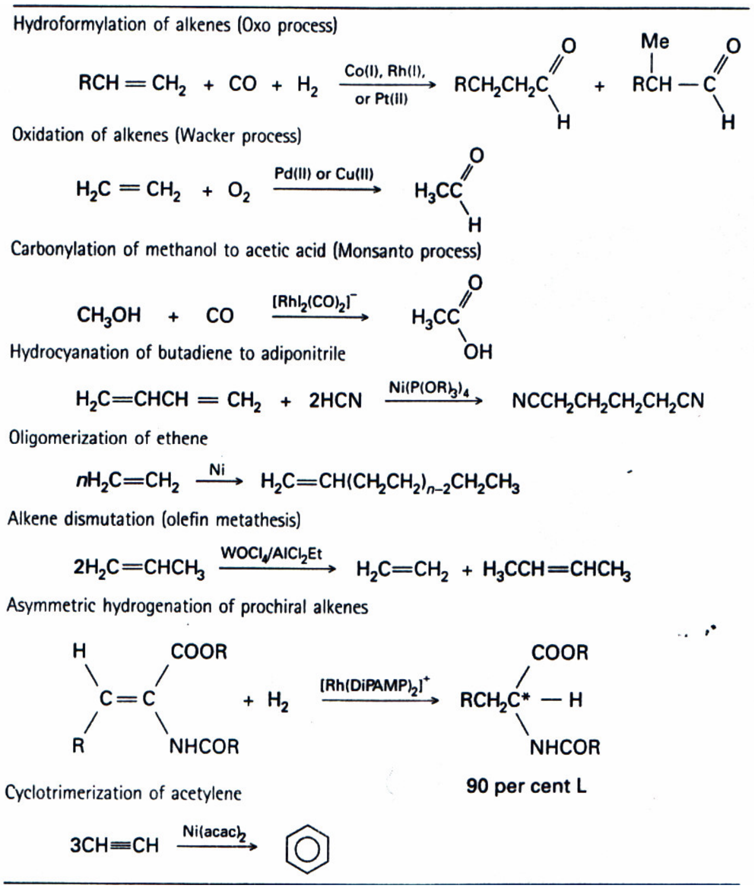
2.4. Homogeneous Catalysts

A homogeneous catalyst is one so dispersed in the solutions that no gross interface exists between it and the reactants. This does not necessarily mean that catalyst and reactant, when alone under reaction conditions, must be in the same physical state. However, when they are not, some agent -e.g., a solvent- must be present to bring them into the same phase, but the solvent is often more than a simple mutualizing agent. It is part, at least a thermodynamic part of the reactants, the catalyst, the product and of the activated complex.

The lattice of heterogeneous catalysts can thus be thought of as a special case of solvent effect. Broadly speaking, solvents themselves are often homogeneous catalysts. Sometimes, if a transition state is less polar than its initial state the reaction can be catalyzed by the entropy gain arising from the liberation of solvent when the transition state forms.[41]

A great variety of dissolved homogeneous catalysts are known: Bronsted and Lewis acids and bases, metal complexes, metal ions, organometallic complexes, organic molecules, enzymes, artificial enzymes, etc. today ‘homogeneous catalysis’ is often used in a restricted sense i.e. to refer to catalysis with organometallic and coordination complexes. This is certainly the area that has led to largest number of industrial applications in the last three decades.[42] Table 2.1 shows some homogeneous catalytic processes.

Table 2.1 Some homogeneous catalytic processes (Adapted from the literature[43])



Hydroformylation of alkenes (Oxo process)

$$RCH{=}CH_2 + CO + H_2 \xrightarrow[\text{or Pt(II)}]{\text{Co(I), Rh(I),}} RCH_2CH_2CHO + RCH(Me)CHO$$

Oxidation of alkenes (Wacker process)

$$H_2C{=}CH_2 + O_2 \xrightarrow{\text{Pd(II) or Cu(II)}} H_3CCHO$$

Carbonylation of methanol to acetic acid (Monsanto process)

$$CH_3OH + CO \xrightarrow{[RhI_2(CO)_2]^-} H_3CCOOH$$

Hydrocyanation of butadiene to adiponitrile

$$H_2C{=}CHCH{=}CH_2 + 2HCN \xrightarrow{Ni(P(OR)_3)_4} NCCH_2CH_2CH_2CH_2CN$$

Oligomerization of ethene

$$nH_2C{=}CH_2 \xrightarrow{Ni} H_2C{=}CH(CH_2CH_2)_{n-2}CH_2CH_3$$

Alkene dismutation (olefin metathesis)

$$2H_2C{=}CHCH_3 \xrightarrow{WOCl_4/AlCl_2Et} H_2C{=}CH_2 + H_3CCH{=}CHCH_3$$

Asymmetric hydrogenation of prochiral alkenes

$$(H)(R)C{=}C(COOR)(NHCOR) + H_2 \xrightarrow{[Rh(DiPAMP)_2]^+} RCH_2C^*(COOR)(NHCOR)-H$$

90 per cent L

Cyclotrimerization of acetylene

$$3CH{\equiv}CH \xrightarrow{Ni(acac)_2} C_6H_6$$

2.5. Heterogeneous Catalysts

Heterogeneous catalysts are used extensively in industry. One attractive feature is that many of these solid catalysts are robust at high temperatures and therefore make available a wide range of operating conditions. Another reason for their widespread use is that extra steps are not needed to separate the product from the catalyst. Typically, gaseous or liquid reactants enter a tubular reactor at one end, pass over a bed of the catalyst, and products are collected at the other end.

Practical heterogeneous catalysts are high-surface-area materials that may contain several different phases and which operate at 1atm or higher pressures. In some cases the bulk of a high-surface-area material serves as the catalyst. One example is the catalytic zeolite ZSM-5, which contains channels through which reacting molecules diffuse. More often multiphasic catalysts are used. These consist of a high-surface-area material that serves as a support on to which an active catalyst is deposited.[34]

2.5.1. Transition Metal Nanoclusters

Nanoclusters, near monodispersed particles that are generally less than 10 nm in diameter have generated intense interest over the past decade. One reason for this is the belief that nanoclusters will have unique properties, derived in part from the fact that these particles and their properties lie between those of bulk and single-particle species. Such 'strange morsels of matter' have many fascinating potential uses, including quantum dots or quantum computers and devices, chemical sensors, light emitting diodes, 'ferrofluids' for cell separations, industrial lithography, and potential as new types of higher activity and selectively catalysts.

Two reasons chemists believe that nanoclusters hold the potential to be more active and selective catalysts than those of today are that a large percentage of a nanocluster's metal atoms lie on the surface, and that surface atoms do not necessarily order themselves in the same way that those in the bulk do. Perhaps most importantly, nanoclusters offer the possibility of controlling both the nanocluster size and the surface ligands in a quantitative, modifiable and better understood way than previously possible for, supported heterogenous catalyst. [44]

2.6. Comparison of Homogeneous and Heterogeneous Catalysts

Each type of the catalysts has its advantages and disadvantages. Heterogeneous catalysts are easily separated from the reaction products (a very positive feature) but tend to require rather high temperatures and pressures and frequently lead to mixtures of products, i.e. they have low selectivity. Homogeneous catalysts must be separated from the product (a negative feature) but operate at low temperatures and pressures (a very positive aspect), and usually give good selectivity (another very positive aspect).[33]

Working in a liquid medium involves not only heat and mass transfer problems that are different from those of heterogeneously catalyzed gas phase reactions, but also introduces solvent recovery and pollution problems. Since the catalysts are expensive and fugitive (because they are molecularly dispersed), their conservation also becomes important. Finally, in trying to contain the system whole new areas of corrosion control are opened. It does seem that most “breakthrough type” industrial processes developed are homogeneously catalyzed ones, these catalysts often seem better understood, more predictable and if we include enzymes more versatile than heterogeneous catalysts.[41]

Table 2.2 Properties of homogeneous and heterogeneous catalysts

PROPERTY	HOMOGENEOUS	HETEROGENEOUS
Solubility	Soluble	Insoluble
Composition	Discrete molecule	Metal deposition on a solid support
Stability	Decompose at high T	Stable at high T
Product separation	Difficult	Easy
Active site	A single active site	Surface
Reaction conditions	Low temperature, low pressure	High temperature, high pressure
Selectivity	Good	Fair
Modification	Easy	Difficult
Investigation	Easy	Difficult

2.7. Problem of Determining the Catalyst; Is It Homogeneous or Heterogeneous?

It is important to be able to distinguish true homogeneous catalysis from soluble (i.e. dispersible) or other metal-particle catalysis because every important catalytic property is influenced differently for these two classes of catalysts: the catalyst's activity, selectivity, stability, lifetime, and recovery.

A variety of experiments have been used to distinguish homogeneous catalysis from heterogeneous catalysis. However, it must be emphasized that there is no single definitive experiment for making this distinction. The experiments used to distinguish true homogeneous catalysis from soluble-metal-particle catalysis are reaction kinetics, transmission electron microscopy, mercury poisoning, CS_2 (or other ligand) poisoning, Crabtree's test, Maitlis' test, Collman's test, light scattering, centrifugation and reactivity patterns.[36]

The ability of Hg(0) to poison metal-particle heterogeneous catalysts, by amalgamating the metal or adsorbing on the metal surface, has been known for more than 80 years[45] and is a widely used test[46]. This experiment is performed by adding Hg(0) to the reaction solution.[47] The suppression of catalysis by Hg(0) is evidence for a heterogeneous catalyst; if Hg(0) does not suppress catalysis, that is an (negative) evidence for a homogeneous catalyst.[50]

Though underutilized, poisoning experiments using added ligands, such as CS_2, PPh_3, and thiophene can be powerful if performed quantitatively.[48] These poisons bind strongly to metal centers, thereby blocking access of the substrate to the active site. If a catalyst can be poisoned completely with $<<1.0$ eq. of the added ligand (per metal atom), that is highly suggestive (kinetic-based) evidence for a heterogeneous catalyst. On the other hand, typically ≥ 1.0 eq. of ligand is required to completely poison homogeneous, monometallic catalysts. [50]

CHAPTER 3

EXPERIMENTAL

3.1. Materials

Ruthenium(III) acetylacetonate, sodium borohydride (98%), tetrahydrofuran (THF) were purchased from Aldrich®. Deionized water was distilled by water purification system (Şimşek SL-200, Ankara, Turkey). All glassware and Teflon coated magnetic stir bars were cleaned with acetone, followed by copious rinsing with distilled water before drying at 150 °C for a few hours.

3.2. Preparation of Ruthenium(III) Acetylacetonate Catalyst

Ruthenium(III) acetylacetonate catalyst was prepared as follows: 0.03 mmol (12 mg) $Ru(acac)_3$ was dissolved in a mixture of 5 mL THF and 5 mL water under vigorous stirring. The solution obtained was dark red in color and stable.

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

The catalytic activity of ruthenium(III) acetylacetonate catalyst in the hydrolysis of sodium borohydride was determined by measuring the rate of hydrogen generation.

For the catalytic activity test, a 75 mL jacketed reaction flask containing a Teflon-coated stir bar was 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. 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 3.1).

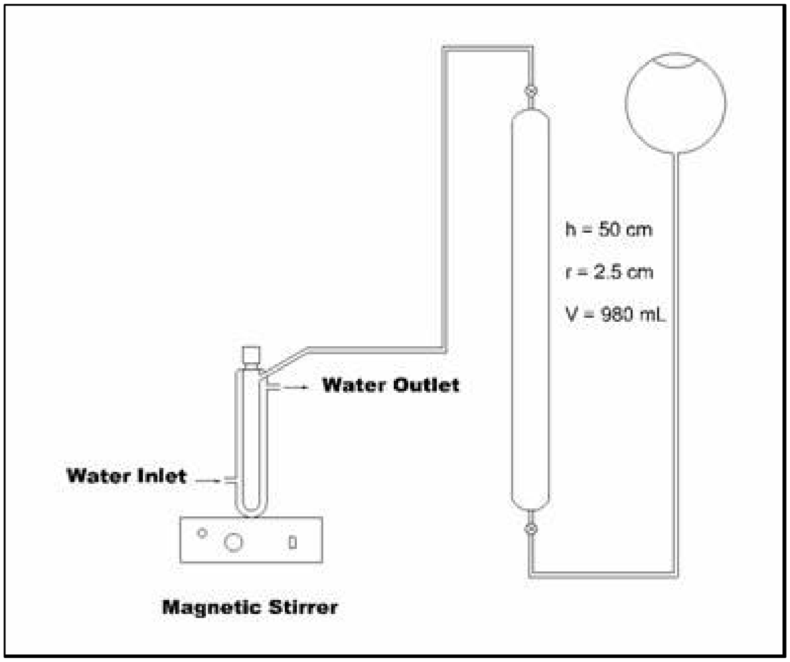


Figure 3.1 The experimental setup used in measuring of the hydrogen generation rate.

After the preparation of experimental setup, 284 mg (7.5 mmol) $NaBH_4$ was dissolved in 40 mL water and the solution was transferred with a 50 mL pipette into the reaction flask thermostated at 25.0 ± 0.1 °C. Then, 10.0 mM

$Ru(acac)_3$ in 10 mL THF/water solution was transferred into the reaction flask using a 10 mL gastight syringe. 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.

3.4. Self Hydrolysis of Sodium Borohydride

In order to determine the self hydrolysis of sodium borohydride, 284 mg (7.5 mmol) sodium borohydride was dissolved in 50 mL water and the solution was transferred with a 50 mL pipette 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.

3.5. Characterization of Ruthenium(III) Acetylacetonate Catalyst In The Hydrolysis of Sodium Borohydride

3.5.1. Infrared Spectra

The infrared spectra of $Ru(acac)_3$ was taken before and after the hydrolysis of sodium borohydride. Firstly, IR spectrum of $Ru(acac)_3$ was taken from KBr pellets on a Nicolet 510 FTIR Spectrophotometer using Omnic software before using it as a catalyst in the reaction. Secondly, after the catalytic reaction, the reaction solution was left for 3 days for precipitation. The collected precipitate was left for drying. Then the FTIR spectrum of precipitate was taken from KBr pellet on a Nicolet 510 FTIR Spectrophotometer using Omnic software.

3.5.2. UV-Visible Spectra

In two glass vials, 10 mL aqueous solution of 0.6 mM Ru(acac)$_3$ (pale red in color) and 10 mL of aqueous solution of 150 mM NaBH$_4$ were prepared separately. Then these two diluted solutions were mixed in quartz cell, final concentrations of Ru(acac)$_3$ and NaBH$_4$ were 0,03 mM and 7.5 mM, respectively. The catalytic reaction was studied by mixing two solutions Absorbance was followed by using a Hewlett Packard 8452A Model Diode Array.

3.6. Poisoning Experiments

To determine whether Ru(acac)$_3$ is a homogeneous or heterogeneous catalyst in the hydrolysis of sodium borohydride, poisoning experiments were performed by using mercury (Hg(0)), carbon disulfide (CS$_2$) and trimethylphosphite (P(OCH$_3$)$_3$).

3.6.1. Mercury Poisoning

Ru(acac)$_3$ was poisoned by Hg(0) in the hydrolysis of sodium borohydride. For this experiment, 6.00 mM Ru(acac)$_3$ used in the hydrolysis of 150 mM sodium borohydride in 50 mL solution was poisoned by 0.12, 0.15, 0.24, 0.30, 0.60, 1.20, 3.00 and 6.00 mM of Hg(0) respectively and the rate of hydrogen generation was measured.

3.6.2. Carbon disulfide Poisoning

Ru(acac)$_3$ was also poisoned by CS$_2$ in the hydrolysis of sodium borohydride. For this experiment, 10.0 mM Ru(acac)$_3$ used in the hydrolysis of 150 mM sodium borohydride in 50 mL solution was poisoned by 0.50, 0.60, 0.75, 1.00, 1.50, 2.00, 5.00 and 10.00 mM of CS_2 respectively and the rate of hydrogen generation was measured.

3.6.3. Trimethylphosphite Poisoning

Another poisoning experiment was performed using $P(OCH_3)_3$ for $Ru(acac)_3$ in the hydrolysis of sodium borohydride. For this experiment, 5.0 mM $Ru(acac)_3$ used in the hydrolysis of 150 mM sodium borohydride in 50 mL solution was poisoned by 0.25, 0.36, 0.50, 1.00, 1.50, 2.50, 3.75 and 5.00 mM of $P(OCH_3)_3$ respectively and the rate of hydrogen generation was measured.

3.7. Kinetic Study of Ruthenium(III) Acetylacetonate Catalyzed Hydrolysis of Sodium Borohydride

In order to establish the rate law for the catalytic hydrolysis of $NaBH_4$ using $Ru(acac)_3$, three different sets of experiments were performed in the same way as described in the section "Catalytic Activity of Ruthenium(III) acetylacetonate in the Hydrolysis of Sodium Borohydride" (3.3). In the first set of experiments, the concentration of $NaBH_4$ was kept constant at 150 mM, and the $Ru(acac)_3$ concentration was varied in the range of 0.40, 0.60, 0.80, 1.00, 2.00, 3.00, 4.00, 5.00, 6.00 and 10.00 mM at 25.0 ± 0.1 °C.

In the second set of experiments, $Ru(acac)_3$ concentration was held constant at 0.60 mM while the $NaBH_4$ concentration was varied in the range of 60, 80, 100, 120, 150, 200, 250 and 300 mM to get various $NaBH_4$ / $Ru(acac)_3$ ratios ($NaBH_4$ / $Ru(acac)_3$ = 100, 133, 167, 200, 250, 333, 417 and 500) 25.0 ± 0.1 °C.

Finally, the catalytic hydrolysis of $NaBH_4$ in the presence of $Ru(acac)_3$ was performed keeping $NaBH_4$ and $Ru(acac)_3$ concentrations constant at various temperatures in the range of 25, 30, 35, 40 and 45 °C in order to obtain the activation energy (E_a), enthalpy of activation ($\Delta H^{\#}$) and entropy of activation ($\Delta S^{\#}$).

3.8. Catalytic Lifetime of Ruthenium(III) Acetylacetonate

The catalytic lifetime of $Ru(acac)_3$ in the hydrolysis of sodium borohydride was determined by measuring the total turnover number (TON). Such a lifetime experiment was started with a 50 mL solution containing 0.6 mM $Ru(acac)_3$ and 450 mM $NaBH_4$ (corresponding to maximum possible total turnover number of 3000) at 25.0 ± 0.1 °C. The hydrolysis of sodium borohydride reaction was continued until hydrogen gas evolution was slowed down to the self hydrolysis level.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1. Ruthenium(III) Acetylacetonate: A Suitable Precursor for the Synthesis of Water Dispersible Ruthenium(0) Nanoclusters?

Transition metal(0) nanoclusters can be prepared from the reduction of a metal salt by using a reducing agent. The nanocluster stabilizer can be present in solution during the reduction so that nanoclusters of certain size are stabilized upon generation. However, it is favorable to have the stabilizer as ligand or anion in the precursor complex, because of its controlled release during the reduction. Such a controlled supply of the stabilizer can provide the formation of nanoclusters in a narrow size distribution (nearly monodispersed). For the synthesis of water dispersible ruthenium(0) nanoclusters, ruthenium(III) chloride has been reduced by sodium borohydride in the presence of acetate ion as stabilizer.[32] As the corresponding ruthenium(III) acetate is not known, a controlled release of acetate ion during the reduction of precursor is not possible. Therefore, we searched for a ruthenium precursor compound bearing a ligand or anion which can act as stabilizer for the ruthenium(0) nanoclusters. Ruthenium(III) acetylacetonate was found to be one of the potential candidate, as acetylacetonate is a strong chelating ligand and, therefore, can also be a good stabilizing agent for ruthenium(0) nanoclusters. As a result of our search, ruthenium(III) acetylacetonate was chosen to be used as an alternative precursor for the synthesis of ruthenium(0) nanoclusters, since it has an anionic ligand, which is soluble in water and can be used as a stabilizer for the Ru(0) nanoclusters in aqueous medium.

The first problem we encountered was the solubility of $Ru(acac)_3$ in water. As determined by the ICP-OES method the solubility of $Ru(acac)_3$ is 5 mg/L in water. To overcome this problem, a mixture of tetrahyrofuran (THF)/water (10% THF and %90 water) was used as solvent. Since sodium borohydride has been used as a reducing agent for the reduction of Ru(III) precursors, it was also used to reduce ruthenium(III) acetylacetonate for the purpose of forming ruthenium(0) nanoclusters. Unexpectedly, we observed that ruthenium(III) acetylacetonate remains unreacted in solution under the experimental conditions even for days. Although, ruthenium(III) acetylacetonate could not be reduced by sodium borohydride under the experimental conditions; as shown by the results of the following analyses, it was surprisingly observed that the hydrolysis of sodium borohydride is catalyzed by this solution, implying that ruthenium(III) acetylacetonate acts as a homogeneous catalyst.

4.1.1. Infrared Spectra

FT-IR spectra of $Ru(acac)_3$ before and after the catalytic hydrolysis of sodium borohydride are displayed together in Figure 4.1. Comparison of IR spectra of $Ru(acac)_3$ before and after the catalytic hydrolysis of sodium borohydride shows that there is no change either in the intensity or in the positions of the absorption bands. This observation indicates that there is no reduction or any change in $Ru(acac)_3$, during the catalytic reaction. In other words, ruthenium(III) acetylacetonate remains unchanged during the reaction.

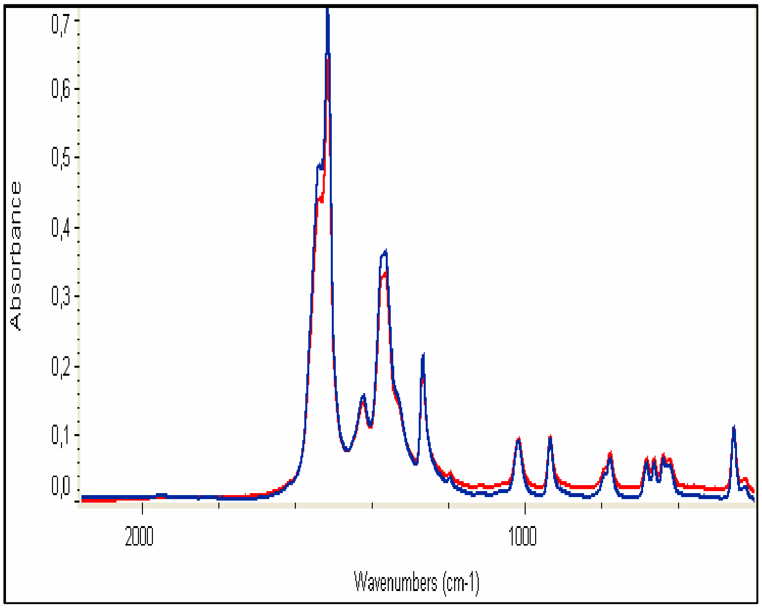


Figure 4.1 FT-IR spectra of Ru(acac)$_3$ before and after the reaction. ([Ru(acac)$_3$] = 3 mM, [NaBH$_4$] = 150 mM, at 25.0 ± 0.1 °C)

4.1.2. UV-Visible Spectra

UV-Visible spectra of Ru(acac)$_3$ were also taken before and after the catalytic hydrolysis of sodium borohydride. As in the IR spectra, the UV-Visible spectra, Figure 4.2, also show that there is no change in the intensity and positions of the absorption bands which means there is no change in of Ru(acac)$_3$ during the catalytic hydrolysis of sodium borohydride.

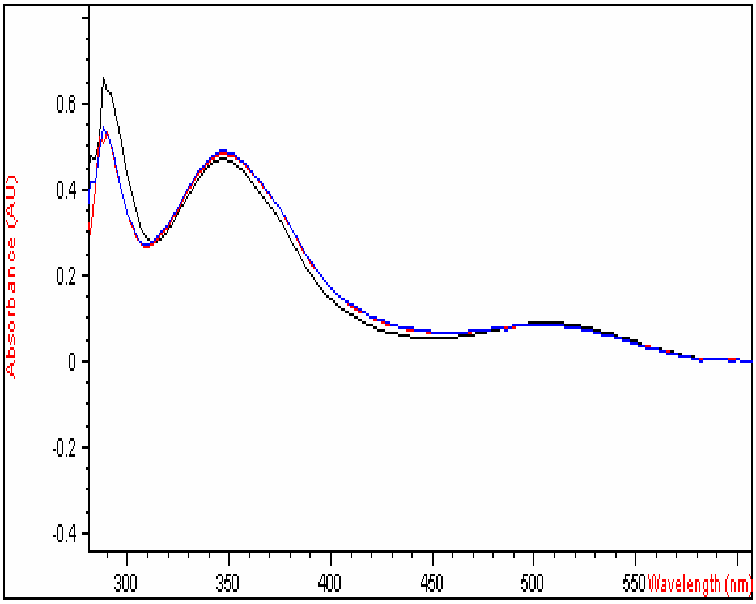


Figure 4.2 UV-Visible spectra of $Ru(acac)_3$ before and after the reaction. ($[Ru(acac)_3]$ = 0.03 mM, $[NaBH_4]$ = 7.5 mM, at 25.0 ± 0.1 °C)

The IR and UV-Vis spectra show that $NaBH_4$ can not reduce Ru(III) to Ru(0) in water when $Ru(acac)_3$ is used as precursor. This can be attributed to the negative reduction potential of $Ru(acac)_3$, -0.51 V.[49] The reduction potential of Ru(III) to Ru(0) in acidic solution is 0.61 V.[34] Thus $Ru(acac)_3$ can not be used as precursor for the synthesis of water dispersable Ru(0) nanoclusters. However the hydrolysis of $NaBH_4$ appears to be catalyzed by $Ru(acac)_3$ as shown by the hydrogen evolution versus time plot in Figure 4.3.

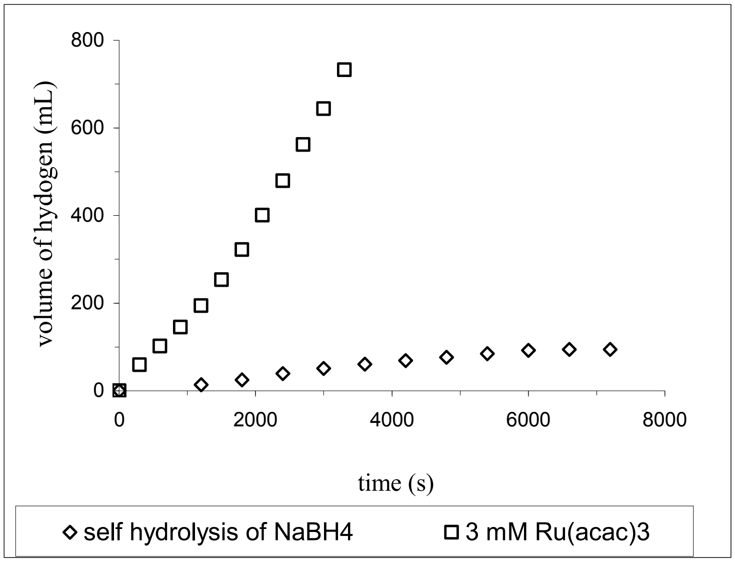


Figure 4.3 Hydrogen evolution versus time plot for the hydrolysis of sodiumborohydride. a) Self hydrolysis, b) catalyzed by ruthenium(III) acetylacetonate ([Ru(acac)$_3$] = 3.0 mM, [NaBH$_4$] = 150 mM, at 25.0 ± 0.1 °C)

4.2. Poisoning Experiments: Determining Whether Ru(acac)$_3$ Catalyst is Homogeneous or Heterogeneous

Catalyst poisoning experiments are essential to determine whether a catalyst is homogeneous or heterogeneous, i.e., whether the true catalyst is a soluble metal complex or water dispersible metal particles.[50] For this purpose Hg(0), CS$_2$ and P(OCH$_3$)$_3$ poisoning experiments were performed.

4.2.1. Mercury Poisoning Experiments

To find whether $Ru(acac)_3$ is homogenous or heterogeneous catalyst in the hydrolysis of sodium borohydride, $Ru(acac)_3$ was poisoned by adding mercury into the catalytic solution and observing the catalytic activity. Figure 4.4 shows the results of nine independent experiments, plotted as the relative rate of hydrogen evolution versus mole ratio of mercury to ruthenium.

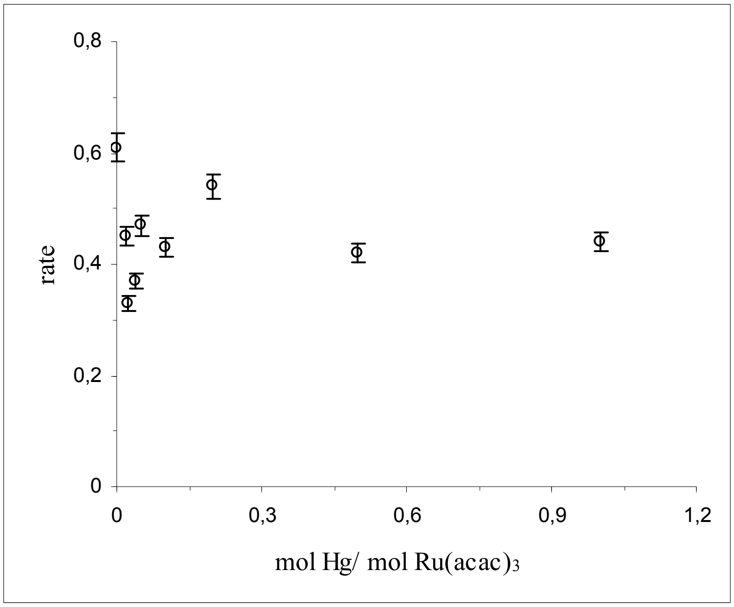


Figure 4.4 Plot of relative rate of hydrolysis of sodium borohydride versus moles of Hg/moles of $Ru(acac)_3$ for the hydrolysis of sodium borohydride. ($[Ru(acac)_3]$ = 6 mM, $[NaBH_4]$ = 150 mM, at 25.0 ± 0.1 °C)

As it is shown in the Figure 4.4, the catalysis was practically not affected by mercury. In other words, the addition of Hg(0) to the reaction solution does not suppress the catalytic activity, which is an evidence for a homogeneous catalyst.[50]

Since the addition of Hg(0) to the reaction solution has no effect on the catalytic activity, it is crucial to perform a control experiment. For this purpose CS_2 and $P(OCH_3)_3$ poisoning experiments were performed.

4.2.2. Carbon Disulfide Poisoning Experiments

$Ru(acac)_3$ catalyzed hydrolysis of sodium borohydride was also poisoned by CS_2. Figure 4.5 shows the results of nine independent experiments, plotted as the relative rate of hydrogen evolution versus the moles of CS_2/the moles of $Ru(acac)_3$.

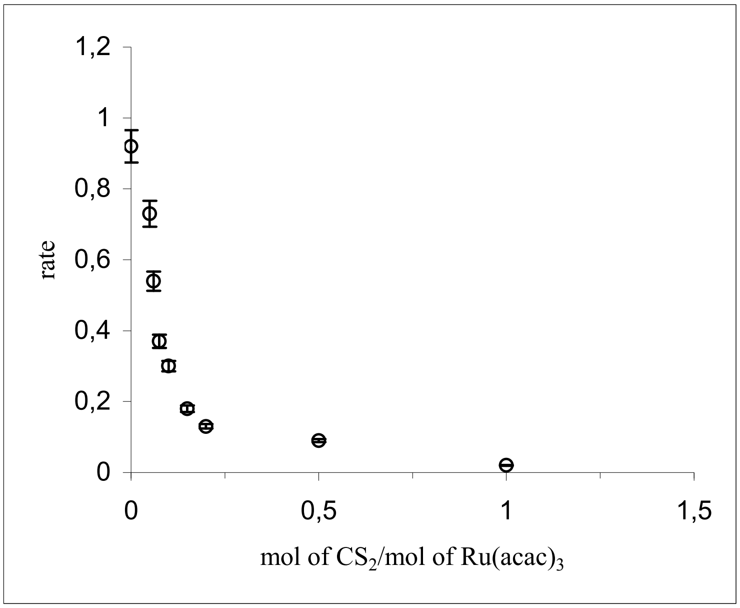


Figure 4.5 Plot of the relative rate versus the moles of CS_2/the moles of $Ru(acac)_3$ for the hydrolysis of sodium borohydride ($[Ru(acac)_3]$ = 10 mM, $[NaBH_4]$ = 150 mM, at 25.0 ± 0.1 °C)

The requirement of one mole of carbondisulfide per mole of ruthenium for a complete poisoning of the catalyst is a compelling evidence for a homogeneous catalyst.[50]

4.2.3. Trimethylphosphite Poisoning Experiments

As a control experiment, $Ru(acac)_3$ catalyzed hydrolysis of sodium borohydride was also poisoned by $P(OCH_3)_3$. Figure 4.6 shows the results of nine independent experiments, plotted as the relative rate of hydrogen evolution versus the moles of $P(OCH_3)_3$/the moles of $Ru(acac)_3$.

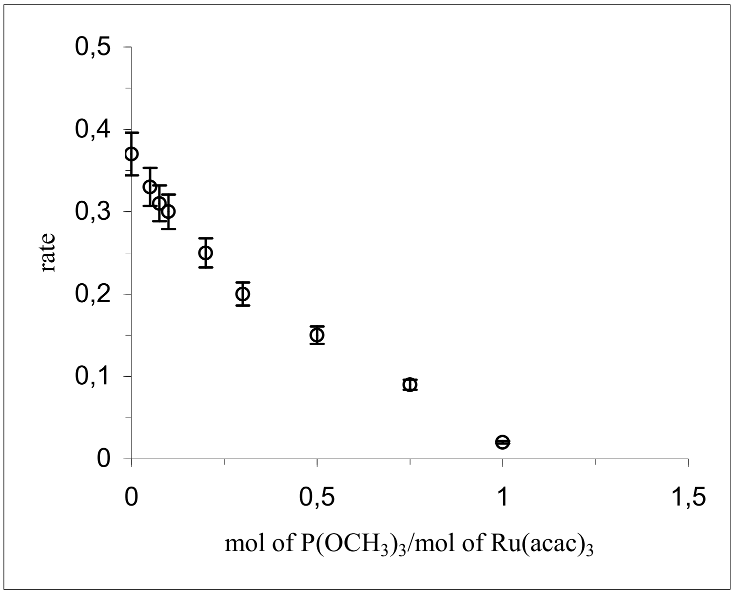


Figure 4.6 Plot of the relative rate versus the moles of $P(OCH_3)_3$/the moles of $Ru(acac)_3$ for the hydrolysis of sodium borohydride ($[Ru(acac)_3]$ = 5 mM, $[NaBH_4]$ = 150 mM, at 25.0 ± 0.1 °C)

As in the CS_2 poisoning experiment, the requirement of one mole of trimethylphosphite per mole of ruthenium for a complete poisoning of the catalyst is a compelling evidence for a homogeneous catalyst.[50]

4.3. Kinetic Study of Ruthenium(III) Acetylacetonate Catalyzed Hydrolysis of Sodium Borohydride

The kinetics of ruthenium(III) acetylacetonate catalyzed hydrolysis of sodium borohydride was studied by monitoring the hydrogen evolution depending on substrate concentration, catalyst concentration and temperature.

$$\mathrm{NaBH_4} + 2\,\mathrm{H_2O} \xrightarrow[\text{THF/water (1:10)}]{\mathrm{Ru(acac)_3}} \mathrm{NaBO_2} + 4\mathrm{H_2O}$$

4.3.1. The Rate Law and Activation Parameters of Ruthenium(III) Acetylacetonate Catalyzed Hydrolysis of Sodium Borohydride

Ruthenium(III) acetylacetonate was used, for the first time, as a homogeneous catalyst in the hydrolysis of sodium borohydride liberating hydrogen gas. Figure 4.7 shows the volume of generated H_2 versus time plots during the $Ru(acac)_3$ catalyzed hydrolysis of 150 mM $NaBH_4$ solution in different concentrations of $Ru(acac)_3$ at 25.0 ± 0.1 °C.

It is seen that $Ru(acac)_3$ has a catalytic activity in the hydrolysis of $NaBH_4$ even at low concentrations and room temperature. The hydrogen evolution starts immediately, without any induction period as the complex added is the true catalyst.

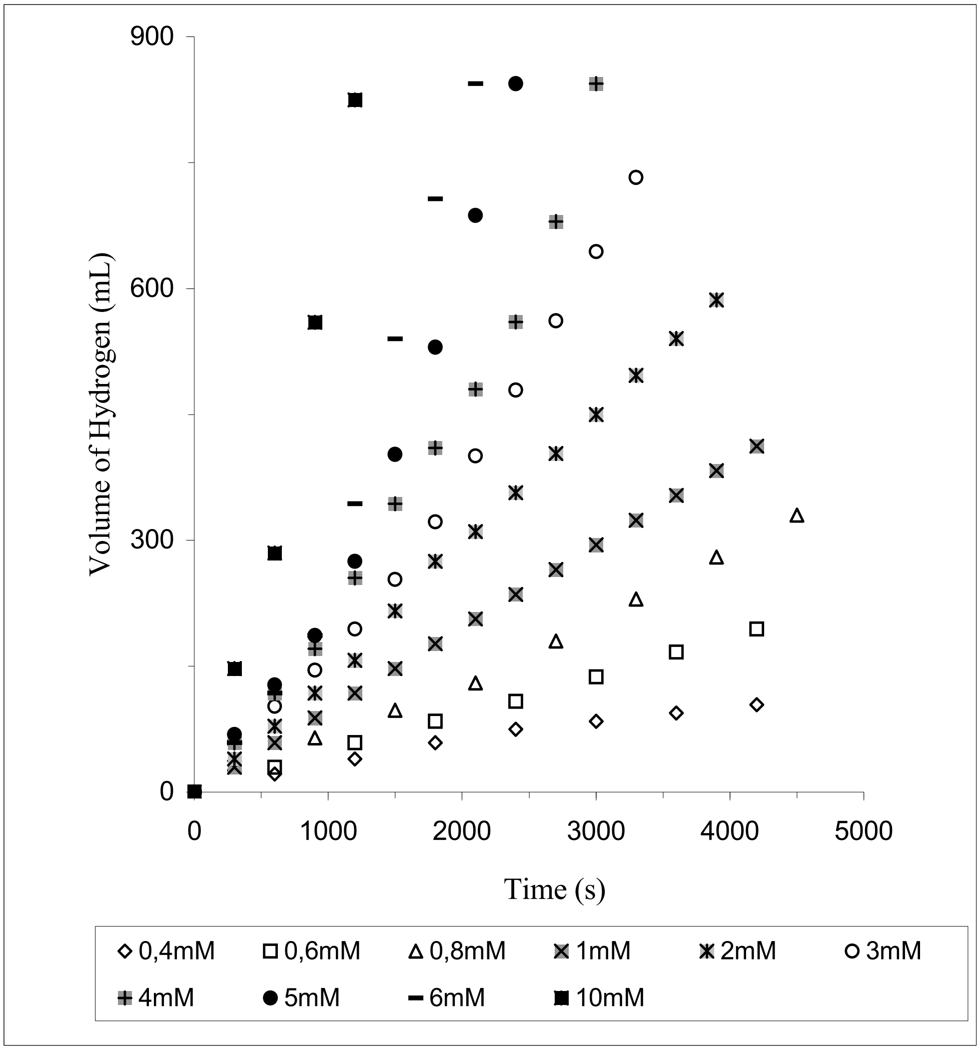


Figure 4.7 Volume of hydrogen generated versus time during Ru(acac)$_3$ catalyzed hydrolysis of sodium borohydride with different Ru(acac)$_3$ concentrations at 25.0 ± 0.1 °C ([NaBH$_4$] = 150 mM)

The hydrogen generation rate was determined from the linear portion of the plot for each experiment with different $Ru(acac)_3$ concentrations. Figure 4.8 shows the plot of hydrogen generation rate versus $Ru(acac)_3$ concentrations, both in logarithmic scale. One obtains a straight line, the slope of which is found to be 1.0646. This indicates that the hydrolysis of sodium borohydride is first order with respect to the concentration of $Ru(acac)_3$.

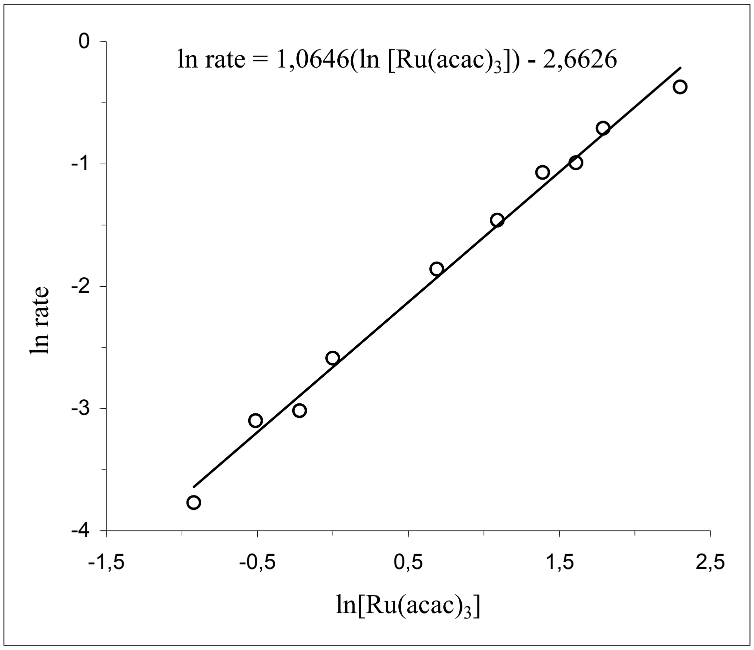


Figure 4.8 The graph of ln (rate) versus ln [Ru] for $Ru(acac)_3$ catalyzed hydrolysis of sodium borohydride

Secondly keeping $Ru(acac)_3$ concentration (0.6 mM) and temperature (25.0 ± 0.1 °C) constant, concentrations of $NaBH_4$ was changed. Figure 4.9 shows the volume of hydrogen generated versus time during $Ru(acac)_3$ catalyzed hydrolysis of sodium borohydride with different $NaBH_4$ concentrations.

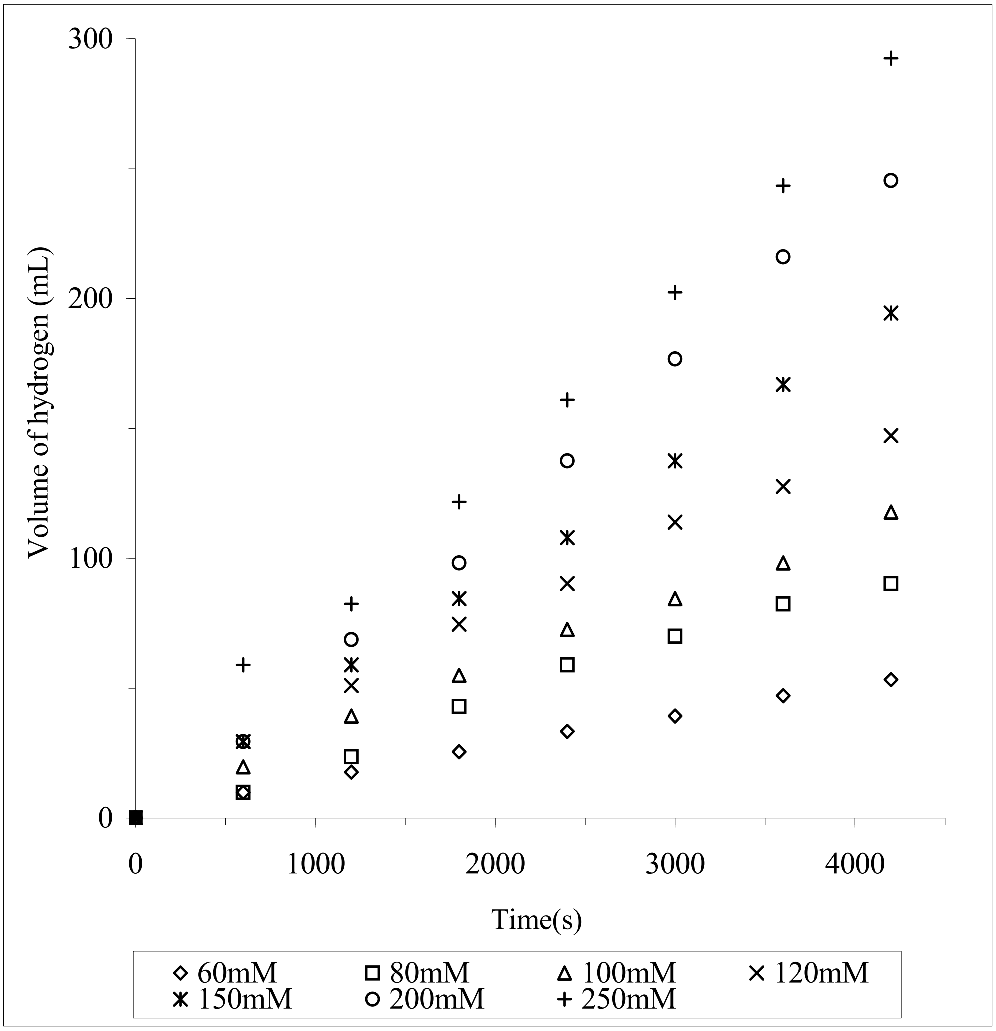


Figure 4.9 Volume of hydrogen generated versus time during $Ru(acac)_3$ catalyzed hydrolysis of sodium borohydride with different $NaBH_4$ concentrations at 25.0 ± 0.1 °C ($[Ru(acac)_3]$ = 0.6 mM)

Figure 4.10 shows the plot of hydrogen generation rate versus $NaBH_4$ concentration. It is seen that $Ru(acac)_3$ catalyzed hydrolysis of sodium borohydride proceeds first order with respect to $NaBH_4$ concentration.

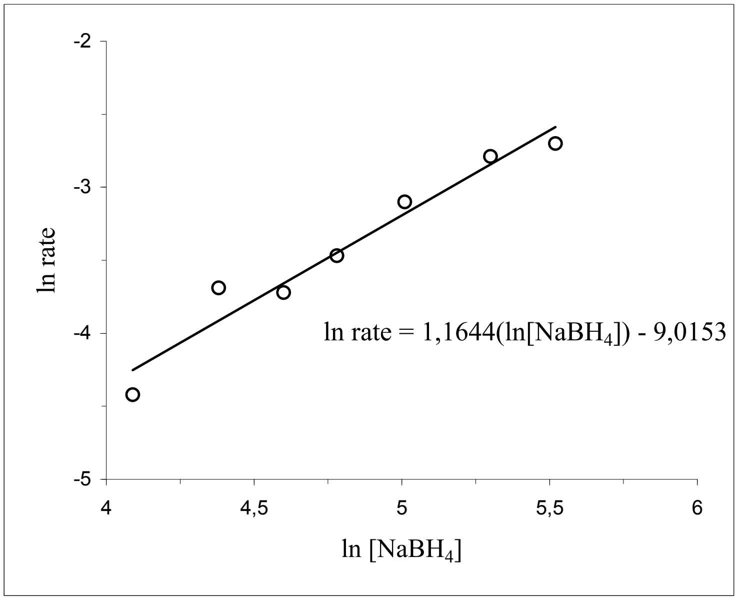


Figure 4.10 The plot of ln (rate) versus ln [NaBH$_4$] for Ru(acac)$_3$ catalyzed hydrolysis of sodium borohydride

$$NaBH_4 + 2\,H_2O \xrightarrow[\text{THF/water (1:10)}]{Ru(acac)_3} NaBO_2 + 4H_2O \qquad \textbf{(Eq. 1)}$$

Thus the rate law for the catalytic hydrolysis of sodium borohydride **(Eq.1)** can be given as:

$$\frac{-4d[NaBH_4]}{dt} = \frac{d[H_2]}{dt} = k[Ru(acac)_3][NaBH_4] \qquad \textbf{(7)}$$

To find the activation parameters, Ru(acac)$_3$ catalyzed hydrolysis of sodium borohydride was studied at five different temperatures, 25, 30, 35, 40 and 45 °C (Figure 4.11). At 45 °C it was observed that Ru(acac)$_3$ was deactivated after 40% conversion. Thus only the results at other four temperatures were used for the evaluation.

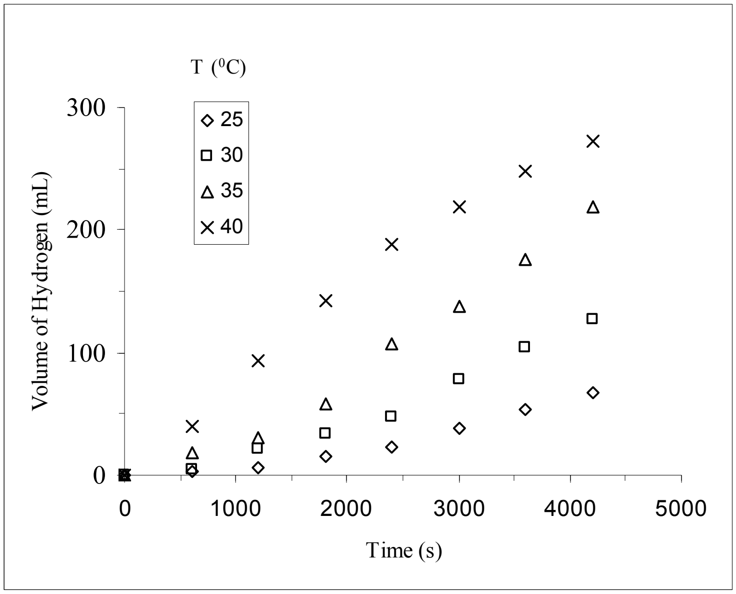


Figure 4.11 Ru(acac)$_3$ catalyzed hydrolysis of sodium borohydride at different temperatures(°C), ([Ru(acac)$_3$] = 0.6 mM, [NaBH$_4$] = 150 mM)

Table 4.1 Rate constants for the hydrolysis of sodium borohydride catalyzed by $Ru(acac)_3$ starting with a solution of 150 mM $NaBH_4$ and 0.6 mM $Ru(acac)_3$ at different temperatures.

Temperature **($^{\circ}$C)**	**Rate Constant, *k*** **($([Ru(acac)_3])^{-1} \cdot s^{-1}$)**
25	2.45×10^{-4}
30	4.53×10^{-4}
35	7.17×10^{-4}
40	7.87×10^{-4}

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

$$k = A.e^{-\frac{E_a}{RT}} \qquad \textbf{(8)}$$

where A and E_a are characteristic constants of the reaction and R is the gas constant. E_a is the Arrhenius activation energy and A is the preexponential factor.[51] When the natural logarithm of equation **8** is taken, the equation becomes:

$$\ln k = \ln A - \left(\frac{E_a}{RT} \right) \qquad \textbf{(9)}$$

In Figure 4.12 the plot of ln k versus $\frac{1}{T}$ gives a straight line with a slope of $\left(-\frac{E_a}{R}\right)$.

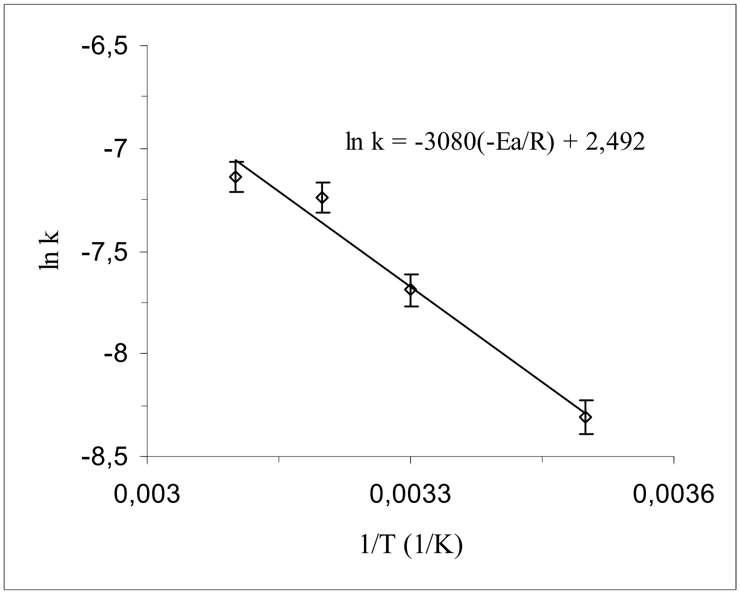


Figure 4.12 Arrhenius plot for the Ru(acac)$_3$ catalyzed hydrolysis of sodium borohydride at different temperatures.

The activation energy, E_a, for Ru(acac)$_3$ catalyzed hydrolysis of sodium borohydride was calculated to be 25.6 ± 1.3 kJ.mol^{-1} using the slope of Arrhenius plot.

To calculate the enthalpy of activation, $\Delta H^{\#}$, and the entropy of activation, $\Delta S^{\#}$, Eyring equation **10** was used by drawing the plot of $\ln\frac{k}{T}$ versus $\frac{1}{T}$ which is shown in Figure 4.13.

$$\ln\frac{k}{T}=\frac{1}{T}\left(-\frac{\Delta H^{\#}}{R}\right)+\ln\frac{k_b}{h}+\frac{\Delta S^{\#}}{R} \qquad \textbf{(10)}$$

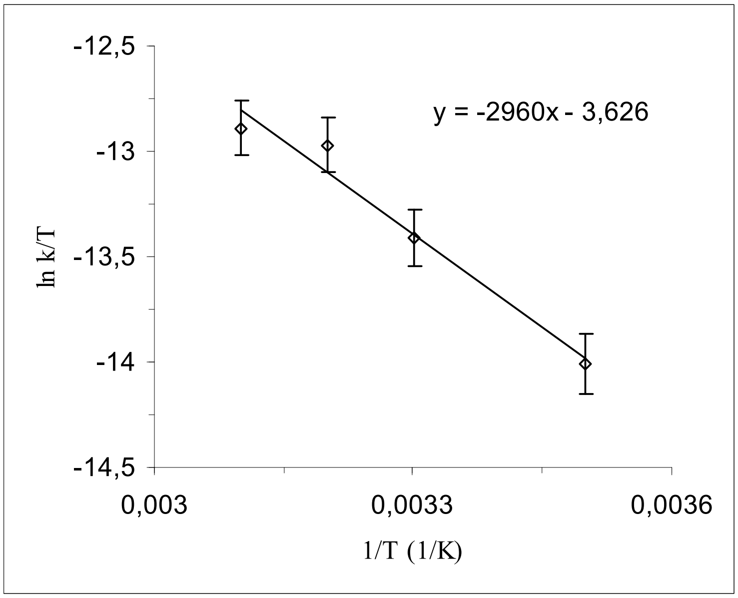


Figure 4.13 Eyring plot for Ru(acac)$_3$ catalyzed hydrolysis of sodium borohydride.

The enthalpy of activation was calculated as 24.6 ± 1.2 $kJ.mol^{-1}$ and the entropy of activation was calculated as -170 ± 5 $J.(mol.K)^{-1}$ for the $Ru(acac)_3$ catalyzed hydrolysis of sodium borohydride using Eyring plot. The small activation enthalpy and the large negative value of activation entropy are indicative of an associative mechanism for the $Ru(acac)_3$ catalyzed hydrolysis of sodium borohydride.

4.4 The Catalytic Life Time of Ruthenium(III) Acetylacetonate

The total turnover number of $Ru(acac)_3$ in the hydrolysis of sodium borohydride was found to be 1183 total turnovers over 180min and turnover frequency of 6.55 min^{-1}.

CHAPTER 5

CONCLUSIONS

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

(i) $Ru(acac)_3$ is not a suitable precursor for the preparation of water-dispersible Ru(0) nanoclusters, as it is not reduced by sodium borohydride

(ii) $Ru(acac)_3$ is an active catalyst in the hydrolysis of sodium borohydride even at low concentration and low temperature.

$$\mathrm{NaBH_4 + 2\,H_2O \xrightarrow[\text{THF/water (1:10)}]{Ru(acac)_3} NaBO_2 + 4H_2O}$$

(iii) $Ru(acac)_3$ is found to be a homogeneous catalyst in the hydrolysis of sodium borohydride.

(iv) In the catalytic hydrolysis of $NaBH_4$ it is found that for $Ru(acac)_3$ is highly active catalyst providing 1183 total turnovers over 180min before they are deactivated. The recorded turnover frequency (TOF) was 6.55 min^{-1}

(v) The rate law for $Ru(acac)_3$ catalyzed hydrolysis of $NaBH_4$ is:

$$\frac{-4d[\mathrm{NaBH_4}]}{dt} = \frac{d[\mathrm{H_2}]}{dt} = k[\mathrm{Ru(acac)_3}][\mathrm{NaBH_4}]$$

(vi) The use of homogeneous Ru(acac)$_3$ catalyst provides the lowest activation energy ever found for the hydrolysis of sodium borohydride, E_a=25.6 ± 1.3 $kJ.mol^{-1}$ as shown in Table 5.1.

Table 5.1 Comparison of activation energy values of some catalysts and Ru(acac)$_3$ for the hydrolysis of sodium borohydride

Catalyst	**Activation Energy (kj.mol^{-1})**
Ru (bulk metal)	47.0 [2]
Co	75.0 [5]
Ni	71.0 [19]
Raney Ni	63.0 [19]
Ru(0) Nanoclusters	41.0 [52]
Ru(acac)$_3$	25.6

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APPENDIX A

The kinetic data of the Ru(acac)$_3$ catalyzed hydrolysis of sodium borohydride studied by monitoring the hydrogen evolution depending on substrate concentration, catalyst concentration and temperature.

Table A.1 Volume of hydrogen generated versus time during Ru(acac)$_3$ catalyzed hydrolysis of sodium borohydride for different Ru(acac)$_3$ concentrations at 25.0±0.1 °C ([NaBH$_4$]=150 mM)

Conc. (mM) **Time (s)**	**0.4**	**0.6**	**0.8**	**1.0**	**2.0**	**3.0**	**4.0**	**5.0**	**6.0**	**10.0**
0	0	0	0	0	0	0	0	0	0	0
300				29.5	39.3	58.9	58.9	68.7	58.9	147.3
600	21.6	29.5	33.4	58.9	78.5	102.1	117.8	127.6	117.8	284.7
900				88.4	117.8	145.3	170.8	186.5	186.5	559.6
1200	39.3	58.9	64.8	117.8	157.0	194.4	255.3	274.9	343.6	824.7
1500				147.3	215.9	253.3	343.6	402.5	540.0	
1800	58.9	84.4	97.5	176.7	274.8	322.0	410.0	530.1	706.8	
2100				206.2	310.2	400.5	480.0	687.2	844.0	
2400	74.7	108.0	129.9	235.6	356.7	479.1	560.0	844.3		
2700				265.1	403.3	561.6	680.0			
3000	84.4	137.4	180.0	294.5	449.8	644.0	844.0			
3300				324.0	496.4	732.4				
3600	94.2	166.9	230.1	353.4	540.3					
3900				382.9	586.3					
4200	104.0	194.4	330.2	412.3						

Table A.2 Volume of hydrogen generated (mL) versus time(s) during Ru(acac)$_3$ catalyzed hydrolysis of sodium borohydride for different NaBH$_4$ concentrations at 25.0±0.1 °C ([Ru(acac)$_3$]= 0.6 mM)

Conc. (mM) / **Time (sec)**	**60**	**80**	**100**	**120**	**150**	**200**	**250**	**300**
0	0	0	0	0	0	0	0	0
600	9.8	9.8	19.6	29.5	29.5	29.5	58.9	53.1
1200	17.6	23.5	39.3	51.0	58.9	68.7	82.5	98.0
1800	25.5	43.0	55.0	74.6	84.4	98.2	121.7	135.5
2400	33.4	59.0	72.6	90.3	108.0	137.4	161.0	166.8
3000	39.3	70.0	84.4	113.9	137.4	176.7	202.4	198.3
3600	47.1	82.5	98.2	127.6	166.9	216.0	243.5	241.5
4000	53,3	90.3	117.8	147.2	194.4	245.4	292.6	276.8

Table A.3 **A)** The volume of hydrogen (mL) versus time(s) for ruthenium(III) acetylacetonate catalyzed hydrolysis of sodium borohydride for constant Ru(acac)$_3$ and NaBH$_4$ concentrations, [Ru(acac)$_3$] =0.6 mM, [NaBH$_4$]=150 mM, at different temperatures (25-40 ^{o}C) **B)** The volume of hydrogen (mL) versus time(s) for self hydrolysis of sodium borohydride (150 mM) at different temperatures (25-40 ^{o}C)

		25 ^{o}C			**30 ^{o}C**	
Time(s)	**A**	**B**	**A-B**	**A**	**B**	**A-B**
600	34.25	31.21	3.04	39.3	34.7	4.62
1200	58.9	52.02	6.88	84.4	62.4	21.9
1800	84.4	69.36	15.04	123.7	90.2	33.5
2400	108.0	84.96	23.04	165.0	117.9	47.1
3000	137.4	98.82	38.58	214.0	135.2	78.8
3600	166.9	112.7	54.20	257.2	152.6	104.6
4200	194.4	126.5	67.90	296.5	169.9	126.6

		35 ^{o}C			**40 ^{o}C**	
Time	**A**	**B**	**A-B**	**A**	**B**	**A-B**
600	34.25	52.0	18.7	117.8	78.0	39.8
1200	58.9	100.6	30.9	231.7	138.7	93.0
1800	84.4	140.6	57.7	333.8	190.7	143.1
2400	108.0	171.7	107.1	421.1	232.4	188.7
3000	137.4	199.4	138.3	490.7	271.1	219.6
3600	166.9	220.2	176.4	555.3	306.9	248.4
4200	194.4	232,4	219.2	614.6	342.7	271.9