



## Ruthenium(III) acetylacetonate: A homogeneous catalyst in the hydrolysis of sodium borohydride

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### ABSTRACT

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. Poisoning experiments with mercury and trimethylphosphite provide compelling evidence for the fact 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;  $E_a = 58.2 \pm 2.6 \text{ kJ mol}^{-1}$ , the enthalpy of activation;  $\Delta H^\ddagger = 55.7 \pm 2.5 \text{ kJ mol}^{-1}$  and the entropy of activation  $\Delta S^\ddagger = 118 \pm 5 \text{ J mol}^{-1} \text{ K}^{-1}$ . Ruthenium(III) acetylacetonate was found to be highly active catalyst providing 1200 turnovers over 180 min in hydrogen generation from the hydrolysis of sodium borohydride before deactivation.

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### 1. Introduction

Modern transition-metal nanoclusters [1] can be stabilized by anionic-ligand [2] and commonly prepared from the reduction of a metal salt in the presence of stabilizer in solution. However, it is favorable to have the stabilizer as ligand or anion in the precursor compound, 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) [3] which are active catalyst for many reactions such as olefin hydrogenation. 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 [4]. Acetate ion was found to be the good stabilizer for the ruthenium(0) nanoclusters catalyst which are also highly active for the hydrolysis of sodium borohydride [5]. Ruthenium(III) acetate appears to be an ideal precursor for the preparation of ruthenium(0) nanoclusters because (i) it will eliminate any other anion such as chloride, (ii) it will provide a controlled release of acetate ion during the reduction of precursor. Unfortunately, the corresponding ruthenium(III) acetate is not known or available. 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,  $\text{Ru}(\text{acac})_3$ , was found to be one of the potential candidates, 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  $\text{Ru}(0)$  nanoclusters in aqueous medium. The first problem we encountered was the low solubility of  $\text{Ru}(\text{acac})_3$  in water, which does not permit any application in aqueous solution. As determined by the ICP-OES method the solubility of  $\text{Ru}(\text{acac})_3$  is 5 mg/L in water. To overcome this problem, a mixture of tetrahydrofuran (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 ruthenium(III) precursors [4,5], 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 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. Here, we report the results of our study on the use of ruthenium(III) acety-

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lactonate as homogeneous catalyst in the hydrolysis of sodium borohydride.

## 2. Experimental

### 2.1. General

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. IR spectra were taken from KBr pellets on a Nicolet 510 FTIR Spectrophotometer using Omnic software. UV–vis electronic absorption spectra were taken on a Hewlett Packard 8452A Model Diode Array spectrophotometer.

### 2.2. Catalytic hydrolysis of sodium borohydride by using ruthenium(III) acetylacetonate

A solution of ruthenium(III) acetylacetonate catalyst was prepared by dissolving 8.0–200 mg (0.020–0.50 mmol) Ru(acac)<sub>3</sub> in a mixture of 5 mL THF and 5 mL water under vigorous stirring. The solution obtained is dark red in color and stable at room temperature for days.

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. After the preparation of experimental setup, 284 mg (7.5 mmol) NaBH<sub>4</sub> 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, the Ru(acac)<sub>3</sub> solution in 10 mL THF/water was transferred into the reaction flask using a 10 mL gastight syringe, yielding a solution with Ru concentration of 0.40–10.0 mM and sodium borohydride concentration of 150 mM. 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 the graduated glass tube for every 5 min.

### 2.3. Self-hydrolysis of sodium borohydride

The self-hydrolysis of sodium borohydride was performed in the same way as described in the previous section. Sodium borohydride (284 mg, 7.5 mmol) 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 min.

### 2.4. Poisoning experiments

To determine whether Ru(acac)<sub>3</sub> catalyst in the hydrolysis of sodium borohydride is homogeneous or heterogeneous, poisoning experiments were performed by using mercury and trimethylphosphite (P(OCH<sub>3</sub>)<sub>3</sub>). In the poisoning experiment, a solution of 6.00 mM Ru(acac)<sub>3</sub> and 150 mM sodium borohydride

in 50 mL THF/water (1:9) was prepared for the catalytic reaction. The reaction was started after adding the poison (mercury or trimethylphosphite) in various amount to the solution at room temperature. The rate of hydrogen evolution was recorded.

### 2.5. Kinetic study of ruthenium(III) acetylacetonate catalyzed hydrolysis of sodium borohydride

In order to establish the rate law for the catalytic hydrolysis of NaBH<sub>4</sub> using Ru(acac)<sub>3</sub>, 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”. In the first set of experiments, the concentration of NaBH<sub>4</sub> was kept constant at 150 mM, and the Ru(acac)<sub>3</sub> 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)<sub>3</sub> concentration was held constant at 0.6 mM while the NaBH<sub>4</sub> concentration was varied in the range of 60, 80, 100, 120, 150, 200, 250 and 300 mM to get various NaBH<sub>4</sub>/Ru(acac)<sub>3</sub> ratios (NaBH<sub>4</sub>/Ru(acac)<sub>3</sub> = 100, 133, 167, 200, 250, 333, 417 and 500) 25.0 ± 0.1 °C. The third set of experiments were performed by keeping NaBH<sub>4</sub> and Ru(acac)<sub>3</sub> concentrations constant at 150 and 0.60 mM, respectively, and varying the temperature in the range of 25, 30, 35 and 40 °C in order to obtain the activation energy (*E*<sub>a</sub>), enthalpy of activation ( $\Delta H^\ddagger$ ) and entropy of activation ( $\Delta S^\ddagger$ ).

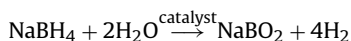
In order to test the reliability of the *k* values, the hydrolysis of sodium borohydride was repeated ten times starting with 150 mM NaBH<sub>4</sub> and 1.0 mM Ru(acac)<sub>3</sub> at 25.0 ± 0.1 °C (exactly under the same conditions). The average *k* value obtained from ten repeat experiments is 0.0876 ± 0.0017 (mol H<sub>2</sub>)/(mol Ru)<sup>-1</sup> s<sup>-1</sup>. Thus the *k* values have a percentage error less than 2%.

### 2.6. Catalytic lifetime of ruthenium(III) acetylacetonate catalyst

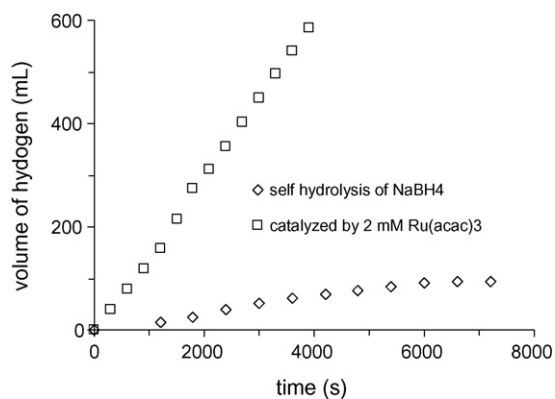
The catalytic lifetime of Ru(acac)<sub>3</sub> in the hydrolysis of sodium borohydride was determined by measuring the total turnover number (TTO). Such a lifetime experiment was started with a 50 mL solution containing 0.6 mM Ru(acac)<sub>3</sub> and 450 mM NaBH<sub>4</sub> (corresponding to maximum 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.

## 3. Results and discussion

Ruthenium(III) acetylacetonate was found to catalyze the hydrolysis of sodium borohydride at room temperature.

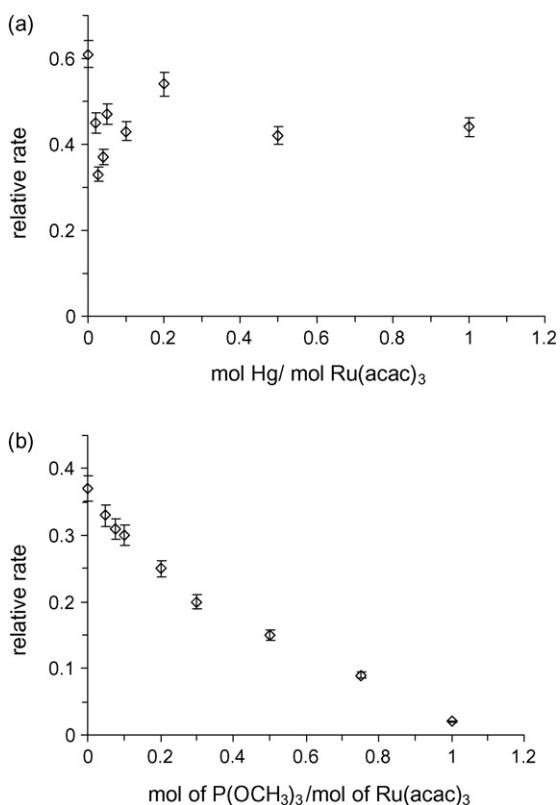


The reaction could be followed by measuring the volume of hydrogen gas evolved from the reaction. Fig. 1 shows the hydrogen generation from the hydrolysis of 150 mM sodium borohydride solution, catalyzed by 2.0 mM Ru(acac)<sub>3</sub>, along with the self-hydrolysis of sodium borohydride at 25.0 ± 0.1 °C. The reaction is accelerated from 0.85 mL H<sub>2</sub>/min for self-hydrolysis to 12 mL H<sub>2</sub>/min for the catalyzed one, an enhancement by a factor of 15. That the hydrolysis of sodium borohydride starts immediately without induction period is indicative of a preformed catalyst, that is, the added Ru(acac)<sub>3</sub> acts as catalyst. The ruthenium containing solid residue isolated from the catalytic reaction was identified as Ru(acac)<sub>3</sub> by means of FTIR and UV–vis electronic absorption spectroscopy. Thus, ruthenium(III) remains unchanged after the catalytic reaction. Poisoning experiments [6] with mercury and

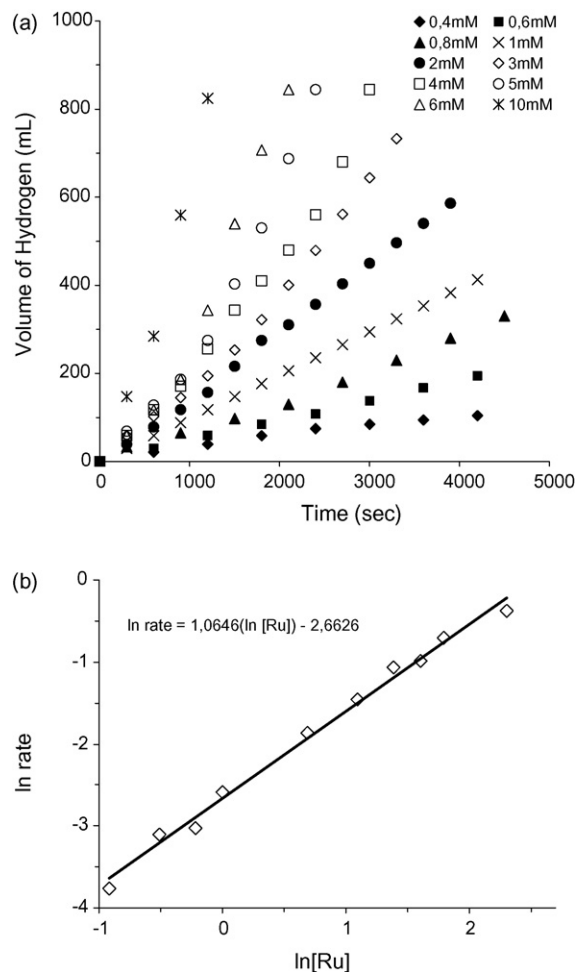


**Fig. 1.** Hydrogen evolution versus time plot for the hydrolysis of sodium borohydride solution ( $[\text{NaBH}_4] = 150 \text{ mM}$ ) at  $25.0 \pm 0.1 \text{ }^\circ\text{C}$ : (a) self-hydrolysis, (b) catalyzed by ruthenium(III) acetylacetonate ( $[\text{Ru}(\text{acac})_3] = 2.0 \text{ mM}$ ).

trimethylphosphite shows unequivocally that ruthenium(III) acetylacetonate acts as homogeneous catalyst. Fig. 2 exhibits the effect of adding the poison (mercury or trimethylphosphite) into the reaction solution on the catalytic activity. While no meaningful change in the catalytic activity is observed upon addition of mercury up to 1.0 equivalent into the reaction solution during the catalytic hydrolysis of sodium borohydride, the rate of catalytic reaction decreases almost linearly with the addition of trimethylphosphite and ultimately stops when one equivalent of poison is added. This result is a compelling evidence for a homogenous catalyst.



**Fig. 2.** Plot of the relative rate of hydrogen evolution versus the equivalent of poison per ruthenium (moles of poison/moles of Ru) for the hydrolysis of sodium borohydride catalyzed by ruthenium(III) acetylacetonate at  $25.0 \pm 0.1 \text{ }^\circ\text{C}$  ( $[\text{Ru}(\text{acac})_3] = 6 \text{ mM}$ ,  $[\text{NaBH}_4] = 150 \text{ mM}$ ): (a) using metallic mercury, Hg as poison, (b) trimethylphosphite,  $\text{P}(\text{OCH}_3)_3$  as poison.

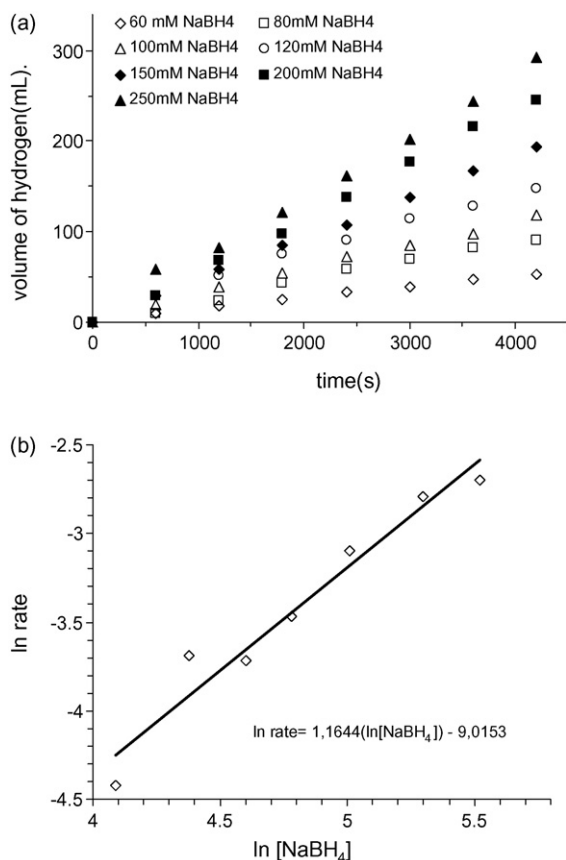


**Fig. 3.** (a) Volume of hydrogen generated versus time for the hydrolysis of sodium borohydride catalyzed by ruthenium(III) acetylacetonate with different  $[\text{Ru}]$  concentrations at  $25.0 \pm 0.1 \text{ }^\circ\text{C}$  ( $[\text{NaBH}_4] = 150 \text{ mM}$ ). (b) The graph of  $\ln(\text{rate})$  versus  $\ln[\text{Ru}]$  for the same reaction.

As a homogeneous catalyst ruthenium(III) acetylacetonate catalyzes the hydrolysis of sodium borohydride liberating hydrogen gas. The homogeneous  $\text{Ru}(\text{acac})_3$  catalyst can provide 1200 turnovers over 180 min in hydrogen generation from the hydrolysis of sodium borohydride before deactivation at room temperature.

Fig. 3 shows the volume of generated H<sub>2</sub> versus time plots during the  $\text{Ru}(\text{acac})_3$  catalyzed hydrolysis of 150 mM NaBH<sub>4</sub> solution in different concentrations of  $\text{Ru}(\text{acac})_3$  at  $25.0 \pm 0.1 \text{ }^\circ\text{C}$ . It is seen that  $\text{Ru}(\text{acac})_3$  has a catalytic activity in the hydrolysis of NaBH<sub>4</sub> even at low concentrations and room temperature. The hydrogen evolution starts immediately, without induction period as the performed catalyst was used. The hydrogen generation rate was determined from the linear portion of the plot for each experiment with different  $\text{Ru}(\text{acac})_3$  concentration. Fig. 3b shows the plot of hydrogen generation rate versus the ruthenium concentrations, both in logarithmic scale. One obtains a straight line, the slope of which is found to be 1.06. This indicates that the catalytic hydrolysis of sodium borohydride is first order with respect to the catalyst concentration.

The effect of substrate concentration on the hydrogen rate was determined by varying the concentration of NaBH<sub>4</sub> at a constant ruthenium concentration of 0.60 mM and temperature of  $25.0 \pm 0.1 \text{ }^\circ\text{C}$  (Fig. 4). The plot of hydrogen generation rate versus NaBH<sub>4</sub> concentration in Fig. 4b gives a straight line with a slope of 1.16. Thus, the  $\text{Ru}(\text{acac})_3$  catalyzed hydrolysis of sodium borohydride is first order with respect to the substrate concentration.



**Fig. 4.** (a) Volume of hydrogen generated versus time for the hydrolysis of sodium borohydride catalyzed by ruthenium(III) acetylacetonate with different  $[\text{NaBH}_4]$  concentration at  $25.0 \pm 0.1$  °C ( $[\text{Ru}(\text{acac})_3] = 0.6$  mM). (b) The graph of  $\ln(\text{rate})$  versus  $\ln[\text{NaBH}_4]$  for the same reaction.

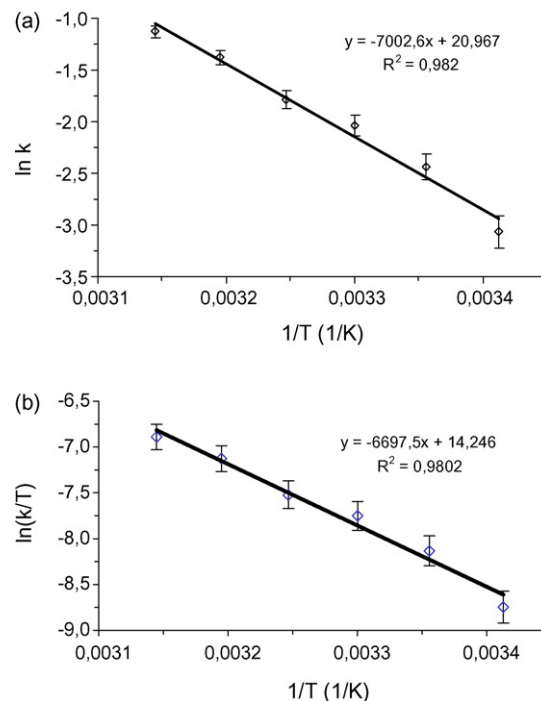
hydride is also first order with respect to NaBH<sub>4</sub> concentration. This first order dependence on the substrate concentration is different from the one observed in the case of heterogeneous catalyst, where the reaction rate is zero order with respect to substrate concentration [5]. The first order dependence of the rate on both the catalyst and the substrate concentration may be attributed to a possible rate-determining step involving the association of borohydride anion with the catalyst.

The hydrolysis of sodium borohydride was carried out at various temperature in the range of 20–45 °C starting with the initial substrate concentration of 150 mM NaBH<sub>4</sub> and an initial catalyst concentration of 1.0 mM ruthenium(III) acetylacetonate. The values of the rate constant  $k$  determined at six different temperatures are listed in Table 1 and used to create the Arrhenius and Eyring plots shown in Fig. 5. The Arrhenius activation energy was found to be  $58.2 \pm 2.6$  kJ mol<sup>-1</sup> for the hydrolysis of sodium boro-

**Table 1**

Values of the rate constant  $k$  in  $(\text{mol H}_2) \cdot (\text{mol Ru})^{-1} \text{ s}^{-1}$  for the hydrolysis of sodium borohydride (150 mM) catalyzed by ruthenium(III) acetylacetonate (1 mM Ru) at different temperatures

$T$ [K]	$k$ $[(\text{mol H}_2) \cdot (\text{mol Ru})^{-1} \text{ s}^{-1}]$
293	$0.0466 \pm 0.0009$
298	$0.0876 \pm 0.0017$
303	$0.130 \pm 0.0026$
308	$0.167 \pm 0.0033$
313	$0.251 \pm 0.0050$
318	$0.324 \pm 0.0065$



**Fig. 5.** (a) Arrhenius plot, (b) Eyring plot for the ruthenium(III) acetylacetonate catalyzed hydrolysis of sodium borohydride at different temperatures. The rate constant at each temperature was determined for the hydrolysis starting with  $[\text{NaBH}_4] = 150$  mM and  $[\text{Ru}] = 1.0$  mM.

hydride catalyzed by ruthenium(III) acetylacetonate. This value is greater than the activation energy of the same reaction reported for ruthenium(0) nanoclusters ( $42$  kJ mol<sup>-1</sup>) [5] and the value reported for the palladium catalyzed hydrolysis ( $28$  kJ mol<sup>-1</sup>) [7]. However, it is still lower than the values reported for the different bulk metal catalysts:  $75$  kJ mol<sup>-1</sup> for cobalt,  $71$  kJ mol<sup>-1</sup> for nickel and  $63$  kJ mol<sup>-1</sup> for Raney nickel [8]. The Eyring plot in Fig. 5b provides the activation enthalpy and activation entropy values:  $\Delta H^\ddagger = 55.7 \pm 2.5$  kJ mol<sup>-1</sup> and  $\Delta S^\ddagger = 118 \pm 5$  J (mol K)<sup>-1</sup> for ruthenium(III) acetylacetonate catalyzed hydrolysis of 150 mM sodium borohydride solution. The large positive value of activation entropy is indicative of a dissociative mechanism for the ruthenium(III) acetylacetonate catalyzed hydrolysis of sodium borohydride, in contrast to the mechanism suggested for the acid catalyzed reaction in the literature [9].

#### 4. Conclusions

In summary, our study on ruthenium(III) acetylacetonate catalyst in the hydrolysis of sodium borohydride leads to the following conclusions and insights, some of which were previously unavailable: (i) Ru(acac)<sub>3</sub> 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)<sub>3</sub> is a homogeneous active catalyst in the hydrolysis of sodium borohydride even at low concentration and room temperature. (iii) The ruthenium(III) acetylacetonate catalyzed hydrolysis of sodium borohydride is first order with respect to both catalyst and substrate, different from the heterogeneous catalysis. (iv) Ruthenium(III) acetylacetonate is a highly active homogeneous catalyst providing 1200 turnovers over 180 min in hydrogen generation from the hydrolysis of sodium borohydride before it is deactivated.

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