Kinetics and Mechanism Investigation of the Synthesized Highly Diasteroselective Substituted Tetrahydropyridines in the Presence of La(NO₃)₃.6H₂O as a Catalyst

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Abstract For the first time, kinetics and mechanism of reaction between 4-methyl-benzaldehyde, 4-bromoaniline and methyl acetoacetate is spectrally investigated in the presence of $La(NO_3)_3.6H_2O$ as a catalyst. Based on the experiment data, the overall order of the reaction is two. The second-order rate constant dependency on the temperature was in agreement with the Arrhenius and Eyring equations. The kinetic and thermodynamic parameters of the reaction have been calculated. Furthermore, useful information was obtained from studies of the effect of solvent and concentration of reactants on the reaction mechanism is a rate-determining step (RDS). The proposed mechanism was also confirmed according to the obtained results and the steady state approximation.

Keywords Kinetics · Catalyst · Mechanism · Piperidine

1 Introduction

Multicomponent reaction (MCR) is a chemical reaction which three or more compounds react to form a single product. The major advantages of MCRs include lower costs, shorter reaction times, higher atom-economy, energy saving, and avoidance of time consuming expensive purification processes [1–7]. It is the fact that MCRs are generally much more environment friendly, and offer instantaneous access to large compound libraries with diverse functionalities, with the avoidance of protection and deprotection steps, for possible combinatorial surveying of structural variations [8-10].

Tetrahydropyridine is one of the most recognizable structural entities among heterocyclic molecules [11, 12]. Tetrahydropyridine has a six-membered ring similar to cyclohexane with one methylene (CH₂) replaced by secondary amino (NH) group. Many piperidine natural products with substitution on nitrogen and carbons are frequently encountered among lysine-derived alkaloids, for example homoproline [13]. Tetrahydropyridine series c-secretase inhibitors have been evaluated for treatment of Alzheimer's disease (AD) [14]. Some tetrahydropyridines were found to possess high profile biological activities, including cytotoxic and anticancer properties [15].

In recent years, widespread researches on the synthesis of tetrahydropyridines have been reported [16-22]. Tetrahydropyridines and their analogs have received attention owing to their biological activities such as antimalarial [23], antihypertensive [24], antibacterial [25], anticonvulsant, and antiinflammatory agents [26]. Kinetic analyses are often performed in order to refine our understanding of what happens on the molecular level during a chemical reaction. During a kinetic study of an organic reaction, for example, experimental evidence in support of or contrary to a proposed mechanism may force us to think of a more detailed (or even alternative) curved-arrow depiction of a chemical reaction. The goal of any kinetic study is to establish a quantitative relationship between the rate of a reaction and the concentration of reagents or catalysts [27]. Thus, it is simply to follow the disappearance of the starting material or appearance of a product as a function of time. This can be done by measuring the rate of a reaction at vary concentrations of reactants and catalysts in order to determine the kinetic order with respect to a particular reactant and to establish an overall rate law for a reaction with a rate constant.

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The experimental techniques that have been used in kinetics studies to accomplish these measurements are many and varied. Numerous kinetics investigations over a large area of different reactions have previously been reported using the UV-vis technique [28–46]. In our previous work, experimental and theoretical kinetics studies and mechanism investigation have fully been discussed for various reactions [47–59]. Synthesis of substituted tetrahydropyridines by one-pot multicomponent reaction using La(NO₃)₃.6H₂O as a catalyst was reported by MT Maghsoodlou and coworkers [60]. Herein, we were interested in studying about the kinetic of the reaction details of our findings in a comprehensive study are reported in this paper.

2 Experimental

2.1 Chemicals and Apparatus Used

The 4-methylbenzaldehyde (1), 4-bromoanilie (2), methyl acetoacetate (3) and La(NO₃)₃.6H₂O were obtained from Merck (Darmstadt, Germany), Acros (Geel, Belgium) and Fluka (Buchs, Switzerland), and used without further purifications. All extra pure solvent including the acetonitrile and methanol were also obtained from Merck (Darmstadt, Germany). A Cary UV-vis spectrophotometer model Bio-300 with a 10 mm light-path quartz spectrophotometer cell was employed throughout the current work. Optimization concentration of catalyst was chosen, 15×10^{-3} M, in each experiment on the basis of the report in synthesis section

2.2 General Procedure

For the kinetic study of the reaction between 4-methylbenzaldehyde (1), 4-bromoaniline (2) and methyl acetoacetate (3) in the presence of $La(NO_3)_3.6H_2O$ as a catalyst (Fig. 1), first it was necessary to find the appropriate wavelength to follow the absorbance change with time. For this purpose in the first experiment, 2×10^{-2} M solution of reactants (1), (2), and 10^{-2} M solution of reactant (3) and 15×10^{-3} M solution of La(NO₃)₃.6H₂O were prepared in acetonitrile as solvent. The relevant spectrum of each compound was recorded at the wavelength range between 200 and 600 nm. In the second experiment, the reaction mixture was started into a 1 mm quartz spectrophotometer cell with 2×10^{-2} , 2×10^{-2} and 1×10^{-2} M solutions of reactant (1), (2) and (3), respectively along with 15×10^{-3} M La(NO₃)₃.6H₂O with respect to stoichiometry of each compound in the overall reaction. The absorbance changes of mixed solution were recorded until the reaction was finished (Fig. 2). From this, the appropriate wavelength was discovered to be 395 nm. Since at this wavelength, reactants (1), (2), (3) and $La(NO_3)_{3.6}H_2O$ have no relatively absorbance value and it provides the opportunity fully to investigate the kinetic and mechanism of the reaction. Herein, in all the experiments, the UV-vis spectrum of the product was measured over the concentration range $(10^{-3} \text{ M} < \text{M})$ product $<10^{-2}$ M) to confirm a linear relationship between the absorbance and concentrations values. In the third experiment under same concentration with the previous experiment, we followed the increases of the absorbance of the product with time at 25 °C temperature and wavelength 395 nm (Fig. 3 a). As can be seen in Fig. 3 b, the original experimental absorbance curve versus time (dotted line) is exactly fitted to second order theoretical curve (solid line). The second-order rate constant is then automatically calculated using the standard equations within the program at 25 °C [28]. It is obvious that the reaction is the second order. In this case, overall order of rate law can be written as: $\alpha + \beta + \gamma = 2$.

$$rate = k_{ovr} [1]^a [2]^b [3]^{\gamma} [Cat]$$

$$\tag{1}$$

3 Results and Discussion

3.1 Effects of Concentration

In order to obtain partial order of reaction regarding methyl acetoacetate (3), pseudo-order conditions were performed for the reaction. So in the fourth experiment, we followed the kinetics reaction by plotting the UV-vis absorbance versus time at wavelength 395 nm for the reaction between (1) $(2 \times 10^{-2} \text{ M})$, (2) $(2 \times 10^{-2} \text{ M})$ and (3) $(5 \times 10^{-2} \text{ M})$ in the presence of La(NO₃)₃.6H₂O (15 × 10⁻³ M) at 250 °C in acetonitrile. For this case the rate law can be expressed:

rate =
$$k_{ovr} [3]^{\alpha} [2]^{\beta} [1]^{\gamma} [cat]$$

rate = $k_{obs} [3]^{\alpha}$ (2)
 $k_{obs} = k_{ovr} [2]^{\beta} [1]^{\gamma} [cat]$

The infinity absorbance (A_{∞}) , is the absorbance at reaction completion, obtain able from Fig. 4 at t = 300 min. With respect to this value, the zero, first or second curve fittings can be drawn automatically for the reaction using the software [28] associated with the UV-Vis instrument. The original experimental absorbance against time data made a pseudo-second-order available fit curve at 395 nm, which exactly fits the experimental curve (dotted line) displayed in Fig. 4. Herein, observation rate constant (k_{obs}) was automatically calculated for the Eq. (2) by the software associated within the UV-vis instrument. It is obviously that the reaction is of the zero order type with respect to methyl acetoacetate (3), $\alpha = 0$.



8 (Product)

Fig. 1 Proposed mechanism for the reaction between 4-methylbenzaldehyde (1), bromoaniline (2) and methyl acetoacetate (3) in the presence of $La(NO_3)_3.6H_2O$ as a catalyst

To confirm the previous result, using another concentration of methyl acetoacetate (3), the same procedure were applied with concentrations of $(2 \times 10^{-2} \text{ M}, \text{ reactant (1)})$, $(2 \times 10^{-2} \text{ M}, \text{ reactant (2)})$ and $(10^{-3} \text{ M}, \text{ reactant (3)})$ in the presence of La(NO₃)₃.6H₂O (15 × 10⁻³ M). Similar results were obtained and gathered in Table 1.

The partial order of reaction with respect to reactants (1) and (2) cannot find because with apply pseudo-order

conditions for reactants (1) and (2), stoichiometry of these reactants in the overall reaction are not observed (2, 2, 1). Thus, the reaction between 4-methylbenzalde-hyde (1), 4- bromoaniline (2) and methyl acetoacetate (3) in the presence of $La(NO_3)_3.6H_2O$ follows second-order kinetics.

The rate law can be written: So $\alpha = 0$ then,



Fig. 2 Absorption changes versus wavelength for the reaction between 4-methylbenzaldehyde (1) $(2 \times 10^{-2} \text{ M})$, 4-bromoanilie (2) $(2 \times 10^{-2} \text{ M})$ and methyl acetoacetate (3) $(1 \times 10^{-2} \text{ M})$ in the presence of La(NO₃)₃.6H₂O (15 × 10⁻³ M) in acetonitrile



Fig. 3 a The original experimental absorbance curve versus time (*dotted line*) b second pseudo order fit curve (*solid line*) accompanied by the original experimental curve (*dotted line*) for the reaction

To investigate which steps of the proposed mechanism (Fig. 1) could be a rate-determining step, the rate law is written using the final step for the product 8:

$$rate = k_5 \ [I_2][I_3] \tag{3}$$

The steady state assumption can be applied for obtaining the concentration of $[I_2]$ which is generated from the following equations:

$$\frac{\mathbf{d}[I_2]}{\mathbf{d}t} = k_2 \ [2][1] - k_5 \ [I_2][I_3] = 0 \tag{4}$$

$$k_5 [I_2][I_3] = k_2 [2][1]$$
(5)

The value of Eq. (3) can be replaced in the Eq. 1 so the rate equation becomes:

$$rate = k_2 [2][1]$$
 (6)

Equation (6) shows that the overall order of reaction is two and indicates that the second step of the reaction is RDS (since k_2 is the only rate constant which appeared in the Eq. (6)).



between (1) (2 \times 10⁻² M), (2) (2 \times 10⁻² M) and (3) (10⁻² M) in the presence of La(NO₃)₃.6H₂O (15 \times 10⁻³ M) in acetonitrile



Fig. 4 a The original experimental absorbance curve versus time (*dotted line*) **b** second pseudo order fit curve (*solid line*) for the reaction between (1) $(2 \times 10^{-2} \text{ M})$, (2) $(2 \times 10^{-2} \text{ M})$ and (3) $(5 \times 10^{-3} \text{ M})$ in the presence of La(NO₃)₃.6H₂O ($15 \times 10^{-3} \text{ M}$) in acetonitrile

Table 1 Rate constant (k_{obs}) for the reaction between reactants (1), (2), (3) and La(NO ₃) ₃ .6H ₂ O in acetonitrile measured at wavelength 395 nm and 25.0 °C	Number	Concentration (1)	Concentration (2)	Concentration (3)	La(NO ₃) ₃ .6H ₂ O	$k_{\rm obs}~({\rm min}^{-1}.{\rm M}^{-1})$
	1	$(2 \times 10^{-2} \text{ M})$	$(2 \times 10^{-2} \text{ M})$	(10^{-2} M)	$(15 \times 10^{-3} \text{ M})$	1.89
	2	$(2 \times 10^{-2} \text{ M})$	$(2 \times 10^{-2} \text{ M})$	$(5 \times 10^{-3} \text{ M})$	$(15 \times 10^{-3} \text{ M})$	1.71
	3	$(2 \times 10^{-2} \text{ M})$	$(2 \times 10^{-2} \text{ M})$	(10^{-3} M)	$(15 \times 10^{-3} \text{ M})$	1.68

Table 2 Reaction rate constant (k_{ove}) in different temperatures and solvents under the same conditions for the reaction between (1) (2 × 10⁻² M), (2) (2 × 10⁻² M), (3) (5 × 10⁻³ M) and La(NO₃)₃.6H₂O (15 × 10⁻³ M)

$k_{\rm ove} \left({\rm min}^{-1}.{\rm M}^{-2}\right)$								
(λ) (nm)	Solvent	10.0 °C	15.0 °C	20.0 °C	25.0 °C	30.0 °C	35.0 °C	40.0 °C
395	Acetonitrile	493.33	685.50	998.66	1,140.00	1,800.00	2,269.72	2,988.31
395	Methanol:acetonitrile (2:8)	684.66	858.98	1,413.33	1,312.18	2,082.66	2,366.44	2,987.68
395	Methanol:acetonitrile (4:6)	916.66	1,009.35	1,748.66	1,761.24	2,176.66	2,964.13	3,797.67

3.2 Effect of Solvents and Temperature

In order to determine the effect of change in temperature and solvent environment on the reaction rate, various experiments were arranged with different temperatures and solvent under the same conditions with the previous experiment. All the experiments were repeated at seven different temperatures, including 10, 15, 20, 25, 30, 35 and 40 °C for each reaction and the second-order rate constants of reactions were obtained. The reaction at 10 °C needs more time to complete the reaction as compared with other



Fig. 5 Dependence of second order $(\ln k_{ove} = \ln k_2)$ on reciprocal temperature for the reaction between reactants (1), (2) and (3) in the presence of La(NO₃)₃.6H₂O in acetonitrile measured at wavelength 395 nm in accordance with Arrhenius equation

temperatures due to exponentially normally reaction dependent on temperature, as the temperature increased the absorbance increased so the rate of reaction increased From Table 2, we realize that the rate increases as temperature goes up from 10 to 40 $^{\circ}$ C.

Physical and chemical characteristics of solvents can cause variations in many reactions. In fact, changing the solvent has a considerable effect on stability of the reactant and activated complex. So, to finding the solvent effect, lone acetonitrile and a mixture of methanol and acetonitrile (methanol: acetonitrile, 2:8, 4:6) have been used in the experiment. The results, showed that rate of reaction in a with high dielectric constant (acetonitrile solvent $(\varepsilon = 37.5)$) are lower than solvent with lower dielectric constant (mixture of methanol and acetonitrile (methanol: acetonitrile, $2:8(\varepsilon = 36.54)$ and methanol: acetonitrile, 4:6(($\varepsilon = 35.58$)) at all temperatures investigated (Table 2). It could be (1) the catalyst is anionic compound; therefore its performance with solvation inpolar solvents are reduced (2) the stabilization differences of the reactants and the activated complex by the solvent in the transition state. As can be seen in Table 2 the rate of reaction increases in each solvent at higher temperatures. In the studied temperature range, the second-order rate constant $(\ln k_2)$ of the reaction was inversely proportional to the temperature, which is agreement with the Arrhenius Eq. (7):

$$\ln K = \ln A - \frac{E_a}{RT} \tag{7}$$

Table 3 Activation parameters $(\Delta S^{\pm}, \Delta H^{\pm}, \Delta G^{\pm} \text{ and } E_{a})$ using the Arrhenius Eq. (7) and Eyring Eq. (8)

Solvent	$\Delta H^{\ddagger} (\text{kJ.mol}^{-1})$	$\Delta S^{\ddagger} (\text{J.mol}^{-1}\text{K}^{-1})$	$\Delta G^{\ddagger} (\text{kJ.mol}^{-1})$	$E_{\rm a}({\rm kJ.mol}^{-1})$
Acetonitrile	41.665	-45.660	55.271	44.139
Methanol: acetonitril2:8	33.535	-71.512	54.847	37.367
Methanol: acetonitril4:6	32.438	-73.454	54.327	34.910



Fig. 6 a, b Eyring plots according to Eqs. (8) and (9) for the reaction between (1), (2), (3) and La(NO₃)₃.6H₂O in acetonitrile

Table 4 Activation parameters $(\Delta S^{\pm}, \Delta H^{\pm}, \Delta G^{\pm} \text{ and } E_{a})$ using different linearized form of Eyring Eq. (9)

Solvent	ΔH^{\pm} (kJ.mol ⁻¹)	ΔS^{\pm} (J.mol ⁻¹ K ⁻¹)	ΔG^{\ddagger} (kJ.mol ⁻¹)
Acetonitrile	41.677	-45.619	55.272
Methanol: acetonitrile (2:8)	33.461	-71.758	54.844
Methanol: acetonitrile (4:6)	32.486	-73.287	54.326

Rate constants for the reaction at the seven different temperatures for the reaction between (1), (2) and (3) were obtained in acetonitrile and a mixture of methanol and acetonitrile (2:8, 4:6) were plotted against 1/T and the activation energy (*E*a) was calculated from the slope of the Arrhenius plot (as shown in Fig. 5) which shows a good straight line with the slope of $-\frac{E_a}{R}$ as in the Eq. (7) The results are accumulated in Table 3.

On the basis of Eyring Eq. (8):

$$\ln\frac{k}{T} = -\frac{\Delta H^{\ddagger}}{RT} + \frac{\Delta S^{\ddagger}}{R} + \ln\frac{k_B}{h}$$
(8)

That $k_{\rm B}$ Boltzmann's constant, *T* temperature, *h* Planck's constant and *R* universal gas constant.

Figure 6 a was plotted and kinetic parameters were estimated. The activation parameters ΔH^{\pm} (activation enthalpy), ΔS^{\pm} (activation entropy) and ΔG^{\pm} (activation Gibbs energy) were determined using the intercept and slope, respectively. Obtained activation parameters for three solvents are given in Tables 3 and 4.

Also, a different linearized form of Eyring equation (Tln (k_{ovr}/T) vs. T) [61] were examined (Fig. 6 b) to check the comparison between the two methods:

$$T\ln\frac{k}{T} = -\frac{\Delta H^{\ddagger}}{R} + T\left(\frac{\Delta S^{\ddagger}}{R} + \ln\frac{k_B}{h}\right)$$
(9)

The highest activation energy ($E_a = 44.139 \text{ kJ. mol}^{-1}$) was obtained in acetonitrile, which means the reactants need high energy for transition state, while for methanol: acetonitrile 4:6 solvent was smaller that means easier reaction will occur. The value of ΔH^{\pm} are positive means consumes energy in its process. The entropy of activation gives a measure of the inherent probability of the transition state, apart from energetic considerations, formation of the transition state requires the reacting molecules to adopt precise conformations and approach one another at a precise angle [62]. If ΔS^{\pm} is large and negative, indicates a transition state that is more highly ordered than the reactants. The Gibbs free energy was determined using the Eq. (10):

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} + \mathrm{T} \Delta S^{\ddagger} \tag{10}$$

The highest activation Gibbs energy was for acetonitrile solvent that means the reaction will occur harder.

4 Conclusion

The overall order of reaction followed second-order kinetics and the partial order with respect to methyl acetoacetate was one. The second step of proposed mechanism was recognized as a rate-determining step (k_2) and this was confirmed based upon the steady-state approximation. In a solvent with higher dielectric constant the rate of reaction reduced and this can be related to decreases in catalyst performance in polar solvent and the stabilization differences of the reactants and the activated complex by the solvent. The rate of reaction was also accelerated by increasing the temperature and was in agreement with Arrhenius and Eyring equations.

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