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Sucrose catalyzes synthesis of 2-amino-4*H*-chromene: Insight to the kinetics

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ABSTRACT

Sucrose is applied as an efficient catalyst for the three-component reaction consisting of aromatic aldehydes, malononitrile and resorcinol in a mixture of water and ethanol media as green solvents. The advantages of this method are excellent yeild, inexpensive catalyst and more environmentally friendly. Mechanistic insight into the synthesis of 2-amino-4*H*-chromene included spectral kinetics approaches is revealed. From the temperature, concentration and solvent studies, the activation energy (Ea=102 kJmol^{-1}) and the related kinetic parameters ($\Delta G^{\ddagger}$=41 kJmol^{-1}, $\Delta S^{\ddagger}$=195 Jmol^{-1} and $\Delta H^{\ddagger}$=99 kJ mol^{-1}) are calculated. The first step of proposed mechanism is recognized as a rate-determining step (k_1) and this is confirmed based upon the steady-state approximation.

Keywords: Sucrose, Catalyst, Kinetics, Mechanism, Chromene derivatives.

1. Introduction

Chromene (Benzopyran) is an important structural component of many naturally occurring compounds [1]. A particularly interesting group of chromenes are 2-amino-4*H*-chromenes (2-amino-4*H*-benzopyrans) with important group of heterocyclic compounds due to their reactivity, anti-bacterial, anti-microbial, genetic and biological activities have gained much importance [2, 3]. 2-Amino-4*H*-chromenes are of particular utility as they belong to privileged medicinal scaffolds serving for generation of small-molecule ligands with highly pronounced spasmolytic, diuretic, anticoagulant, antibacterial and antianaphylactic activities [4-7]. In addition, they can be used as cognitive enhancers for the treatment of neurodegenerative diseases, including Alzheimer's disease, amyotrophic lateral sclerosis, Huntington's disease, Parkinson's disease, AIDS associated dementia and Down's syndrome as well as for the treatment of schizophrenia and myoclonus [8]. A number of methodologies have been developed to synthesize chromene derivatives with the use of hazardous organic solvents, long reaction time, use of toxic catalysts, and lack of general applicability [9-15]. Moreover, these methods also suffer from the drawbacks such as expensive catalyst, cumbersome condition of the synthesized product. Along with other reaction parameters, the nature of the catalyst plays a significant role in determining yield, selectivity, and general applicability. Thus, development of an inexpensive, mild, general, and reusable catalyst for MCRs remains an issue of interest [16-18].

As a part of our current studies on the development of efficient multi-component reaction for the preparation of interesting bioactive molecules [19-21], herein we report a simple and efficient procedure for the synthesis of highly substituted 2-amino-4*H*-chromenes via a one-pot three-component reaction between benzaldehyde 1, resorcinol 3 and malononitrile 2 in the presence of sucrose as a catalyst in the green solvents as a mixture of ethanol and water (Scheme 1). Sucrose as a clean catalyst, general applicable, inexpensive, and soluble in water and environmentally friendly.
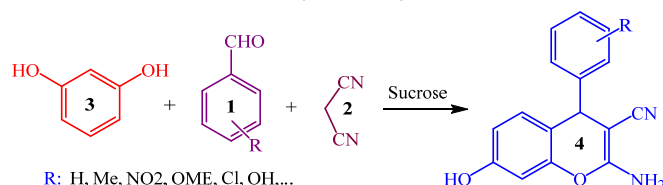
Scheme 1. Synthesis reaction of 2-amino-4*H*-chromene derivatives.

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The other advantages of this method also were excellent yield, and short reaction time reaction. In recent years, we have endeavored to expand experimental and theoretical studies on the kinetics and mechanisms of some organic reactions [22-24]. Herein, we have performed various methods and techniques as UV-Vis spectrophotometry, dynamic ^{1}H NMR and theoretical calculations to elucidate detailed kinetics and mechanisms of these reactions. In this work, for the first time, we describe kinetic results together with detailed mechanistic studies of the synthesis reaction of 2-amino-4*H*-chromenes based on a global kinetic analysis methodology using the UV-Vis spectrophotometry apparatus.

2. Experimental

2.1. General

All reagents and solvents obtained from Fluka and Merck and used without further purification. Sucrose were also obtained from Merck (Darmstadt, Germany), and used without further purification. Melting points was measured on an Electrothermal 9100 apparatus. A Cary UV-Vis spectrophotometer model Bio-300 with a 10 mm light-path quartz spectrophotometer cell was employed throughout the current work.

2.2. General procedure for the synthesis of 2-amino-4H-chromene

A mixture of an aromatic aldehyde 1 (1 mmol), malononitrile 2 (1 mmol), resorcinol 3 (1 mmol) and sucrose (20 mol %) in a mixture of water and ethanol (3:1, 4 mL) was heated for an appropriate length of time. During the procedure, the reaction was monitored by TLC. After completion of the reaction, the mixture was filtrate and the precipitated solid recrystallized from ethanol 95% to give compounds in excellent yields.

3. Results and Discussion

3.1. Optimize the synthesis conditions

In order to optimize the conditions, the reaction between benzaldehyde 1, malononitrile 2, resorcinol 3, and 10 mol% of sucrose as a simple model substrate was undertaken in various conditions. First we tested the effect of amount of the catalyst. As a result, with the mixture of benzaldehyde 1, malononitrile 2 and resorcinol 3 in the presence of 10 mol% sucrose, the product was obtained in 42% yield at 70 °C in water and ethanol (3:1) for 10 hr. Adding amount of catalyst to 20 mol%, 30 mol% and 40 mol%, yields of 80%, 52% and 21% were obtained, respectively. Use of just 20 mol% sucrose is sufficient to push the reaction forward and higher amounts of the catalyst did not improve the result to any greater extent. Thus, 20 mol% was chosen as a suitable amount of catalyst for these reactions (Table 1). In order to optimize the other conditions, the reaction between benzaldehyde 1, malononitrile 2, resorcinol 3, and 20 mol% of sucrose as a simple model substrate was undertaken in various conditions. The effects of various solvents were also investigated on these reactions. It is noteworthy to mention that the polar solvents such as water and ethanol or methanol, afford better yields than nonpolar ones, and a mixture of water and ethanol is the most effective solvent (Table 2).

Table1. Optimization of catalyst in synthesis of 2-amino-4*H*-chromene.

Entry	Catalyst (mol %)	Time (h)	Yield (%)
1	10	10	42
2	**20**	**9**	**80**
3	30	10	52
4	40	10	21

Table 2. Optimization of solvent in synthesis of 2-amino-4*H*-chromene.

Entry	Solvent	Temp. (°C)	Ratio
1	H_2O	85	-
2	**H_2O/EtOH**	**85**	**3:1**
3	H_2O/EtOH	85	3:2
4	H_2O/EtOH	85	1:1
5	EtOH	85	-

In addition, the same model reaction was carried out in a mixture of water and ethanol at different temperatures to assess the effect of temperature to the reaction yield. It was observed that yield was the function of temperature, since the yield increased as the reaction temperature rose, at 85 °C, the product was obtained in an excellent yield and at the higher temperature did not increase the yield (Table 3).

3.2. Kinetic

To gain further insight into the reaction mechanism between benzaldehyde 1, resorcinol 3 and malononitrile 2 in the presence of sucrose, a kinetics study of the reaction was undertaken by UV-Vis spectrophotometry technique. Firstly, it was necessary to find the appropriate wavelength in order to follow the kinetic study of the reaction. For this purpose, in the first experiment, 10^{-3} M solution of each reactant 1, 2, 3 and 2×10^{-4} M solution of sucrose were prepared in a mixture of water and ethanol (3:1) as solvent. Approximately 3 mL aliquot from each reactant was pipetted into a 10 mL light path quartz spectrophotometer cell and the relevant spectrum of each compound at 26 °C was recorded over the wavelength range 200-550 nm. In the second experiment, 0.8 mL aliquot of 8×10^{-4} M solution catalyst and 0.8 mL aliquot of 4×10^{-3} M solution of reactants 1 and 2 were pipetted in to a quartz spectrophotometer cell then 0.8 mL aliquot of 4×10^{-3} M solution of reactant 3 was added to the mixture according to stoichiometry of each reactant in the overall reaction. The reaction was monitored by recording scans of the entire spectra with 10 minute intervals during the whole reaction time at the ambient temperature (Fig. 1). As can be seen in Fig. 1, the appropriate wavelength was discovered to be 345, 340, and 335 nm (corresponding mainly to the product 4a). Since at these wavelengths, reactants 1, 2, 3 and sucrose have relatively no absorbance value, it gave us the chance to find the practical conditions that allows kinetics and a mechanistic investigation of the reaction. Herein, in all the experiments, the UV-Vis spectrum of the product was measured over the concentration range (10^{-4} M $\leq$ M product $\leq 10^{-3}$ M) to confirm a linear relationship between the absorbance and concentrations values. In the third experiment under same concentration of each reactant (10^{-3} M), experimental absorbance curve was recorded versus time at 26 °C temperature and wavelength 340 nm. This is shown in Fig. 2 that the experimental absorbance curve (dotted line) exactly fits to the second order curve (solid line) [25]. It is obvious that the reaction is second order. In this case, overall order of rate low can be written as: $\alpha+\beta+\gamma= 2$.

$$\text{rate} = k_{\text{ovr}}[1]^\alpha[2]^\gamma[3]^\beta[\text{Cat}] \qquad (1)$$

3.3. Mechanism

3.3.1. Effects of concentration

In order to find partial order of reactants 1 and 2 under pseudo-order condition, in the two separate experiments (fourth and fifth experiment), same procedures were employed with these concentrations [(5×10^{-4} M, reactant 1), (10^{-3} M, reactant 2)], [(10^{-3} M, reactant 3)] and sucrose (20%mol) and also [(5×10^{-4} M, reactant 1)], [(5×10^{-4} M, reactant 2), (10^{-3} M, reactant 3)] and sucrose (2×10^{-4} M).

For obtaining equations (2) and (3), the rate law can be expressed:

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

$$\text{rate} = k_{\text{obs}}[1]^\alpha \qquad (2)$$

$$k_{obs} = k_{ove}\,[2]^\beta[3]^\gamma[\text{Cat}]$$

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

$$\text{rate} = k_{\text{obs}}[1]^\alpha[2]^\gamma \qquad (3)$$

$$k_{\text{obs}} = k_{ovr}[1]^\beta[\text{Cat}]$$

The result of fourth experiment (k_{obs}) was different from the fifth experiment. Herein, in the fourth experiment the original experimental absorbance curves versus times provided a pseudo-first order (Fig. 3a). The experimental absorbance curve versus times along with a first-order fit for this experiment was recorded at 340 nm and 26 °C.

Then, the rate constant, of the reactions were automatically obtained by the software program. Herein, according to equation 2, partial order with respect to compound **1** is 1 (α=1). In the fifth the experimental absorbance curve against times along with a second-order fit was obtained (Fig. 3b) at 340 nm and 26 °C. Hence, the total partial orders in relation to equation 3 is $\alpha+ \gamma =2$. In previous experiment (fourth) α was equal to 1. As a result, it is reasonable to accept that the partial order with respect to reactant 2 is one (γ =1). Therefore, with respect to the third experimental result ($\alpha+\beta+ \gamma =2$), fourth experiment (α=1) and the fifth experiment (γ =1) the partial order of β can be determined as zero (β=0). So the experimental rate law can be expressed:

$$\text{rate} = k_{\text{obs}}[1][2] \qquad (3a)$$

$$k_{\text{obs}} = k_I[\text{Cat}]$$

Utilizing the above results, the simplified scheme of the proposed reaction mechanism is shown in Scheme 2. To investigate which steps of the proposed mechanism is a rate-determining step, the rate law was written using the final step of reaction:

$$\text{rate} = k_4[I_3] \qquad (4)$$

Table 3. Optimization of temperature in synthesis of 2-amino-4*H*-chromene.

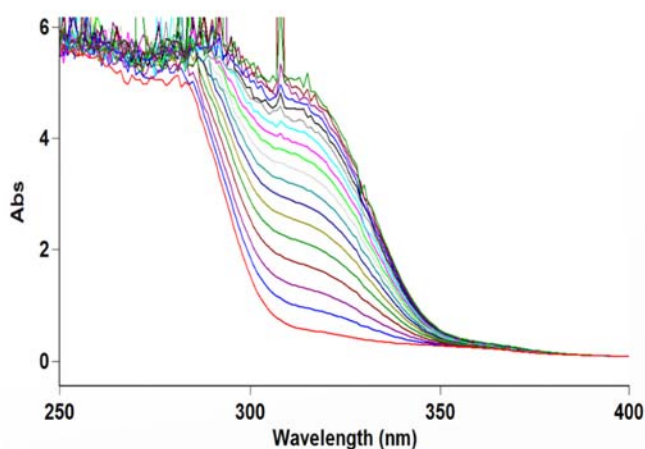| Entry	Temp. (°C)	Catalyst (mol %)	Time (h)
1	50	20	24
2	60	20	24
3	70	20	10
4	**80**	**20**	**9**
5	85	20	8
6	85	20	9

Fig. 1. The UV-Vis spectra of the reaction between benzaldehyde 1 (10^{-3} M), resorcinol 3 (10^{-3} M) and malononitrile 2 (10^{-3} M) in the presence of sucrose (2×10^{-4} M) in a mixture of water and ethanol (3:1) as reaction proceeds into a 10 mm light-path cell. Herein, the upward of direction of the arrow indicate that the progress of product versus times.
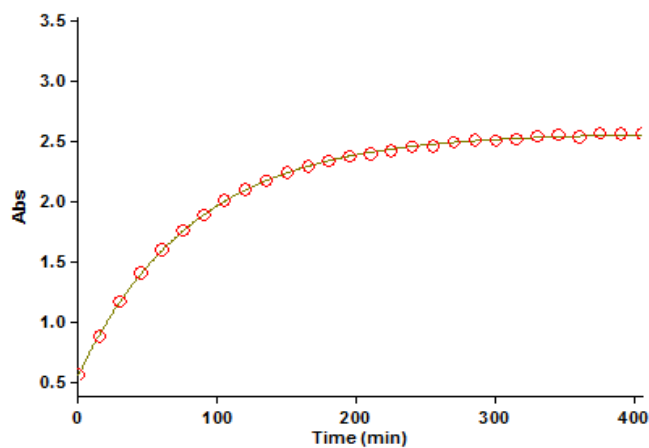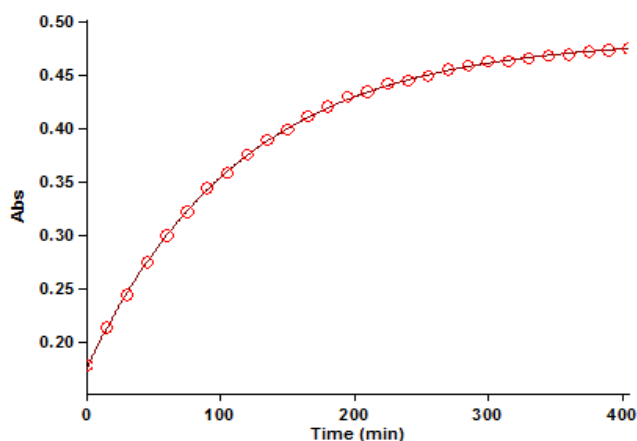

Fig. 2. The experimental absorbance change (dotted line) along with the second order fit curve (solid line) against time for the reaction between benzaldehyde 1 (10^{-3}M), malononitrile 2 (10^{-3} M), resorcinol 3 (10^{-3}M) and sucrose (2×10^{-4} M) at 340 nm, 26 °C and in a mixture of water and ethanol (3:1) [25].
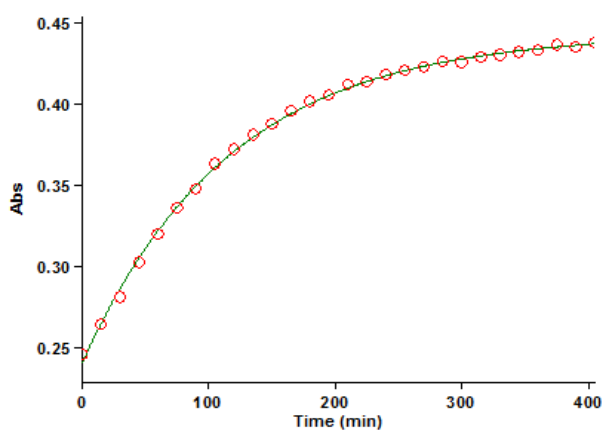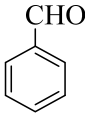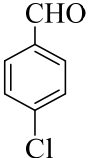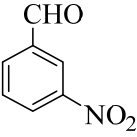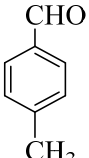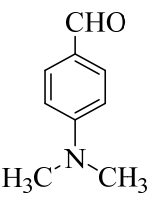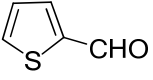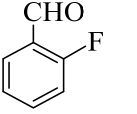

(a)

(b)

Fig. 3. First pseudo order fit curve (solid line) along with the original experimental curve (dotted line) in relation to malononitrile 2, for the reaction between 1 (5×10^{-4} M), 2 (10^{-3}M), 3 (10^{-3} M) and sucrose (2×10^{-4} M) which was processed in a mixture of water and ethanol (3:1) at 26 °C

Table 4. Synthesis of 2-amino-4*H*-chromene derivatives using sucrose.

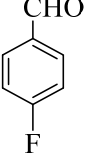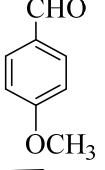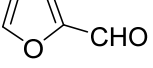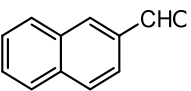| Entry	Derivatives	Product	Time (h)	Yield (%)	m.p (°C) found	m.p (°C) reported	Ref.
1	CHO	**4a**	8	92	229-231	232-234	[16]
2	CHO, Cl	**4b**	8	72	162-163	161-162	[16]
3	CHO, NO$_2$	**4c**	9.5	69	169-171	170-171	[16]
4	CHO, CH$_3$	**4d**	9	67	181-182	184-186	[16]
5	CHO, H$_3$C–N–CH$_3$	**4e**	9.5	69	194-195	189-191	[17]
6	S–CHO	**4f**	8.5	89	188-190	190-191	[17]
7	CHO, F	**4g**	8.5	90	200-201	200-202	[16]
8	CHO, F	**4h**	8	90	186-187	187-189	[16]
9	CHO, OCH$_3$	**4i**	7.5	88	111-114	112-114	[17]
10	O–CHO	**4j**	8	90	186-189	189-191	[17]
11	CHC	**4k**	9	80	228-232	230-232	[1]

The steady state approximation can be applied for obtaining the concentration of $[I_3]$ which is generated from the following equations:

$$\frac{d[I_3]}{dt} = k_3[I_2][Cat^-] - k_4[I_3] = 0 \tag{5}$$

$$k_3[I_2][Cat^-] = k_4[I_3] \tag{6}$$

The value of equation (6) can be replaced in the equation (4) so the rate equation becomes:

$$rate = k_3[I_2][Cat^-] \tag{7}$$

For obtaining the concentration of intermediate $[I_2]$ the following equation is yielded by applying the steady state assumption:

$$\frac{d[I_2]}{dt} = k_2[I_1][3] - k_3[I_2][Cat^-] = 0$$

and $k_2[I_1][3] = k_3[Cat^-][I_2]$ (8)

And with the replacement of the equation 8 in 7 the following equation is obtained:

$$rate = k_2[I_1][3] \tag{9}$$

And we can obtain the value of $[I_1]$ as below which can be replaced in the equation (9) for generation of equation (12):

$$\frac{d[I_1]}{dt} = k_1[1][2][Cat^-] - k_{-1}[I_1][Cat^-][H_2O] - k_2[I_1][3] = 0 \tag{10}$$

$$k_1[1][2][Cat] = [I_1](k_{-1}[Cat^-][H_2O] + k_2[3]) \tag{11}$$

$$rate = k_2[3]\frac{k_1[1][2][Cat]}{k_{-1}[H_2O][Cat-] + k_2[3]} \tag{12}$$

Equation (12) is not compatible with the experimental data, therefore the rate constants k_{-1} and k_2 has no chance to be a rate determining step, nevertheless if $k_2[3] \gg k_{-1}[H_2O][Cat^-]$, the following equations can be obtained:

$$rate = k_1[1][2][Cat] \tag{13}$$

$$k_{obs} = k_1[Cat] \tag{14}$$

$$rate = k_{obs}[1][2] \tag{15}$$
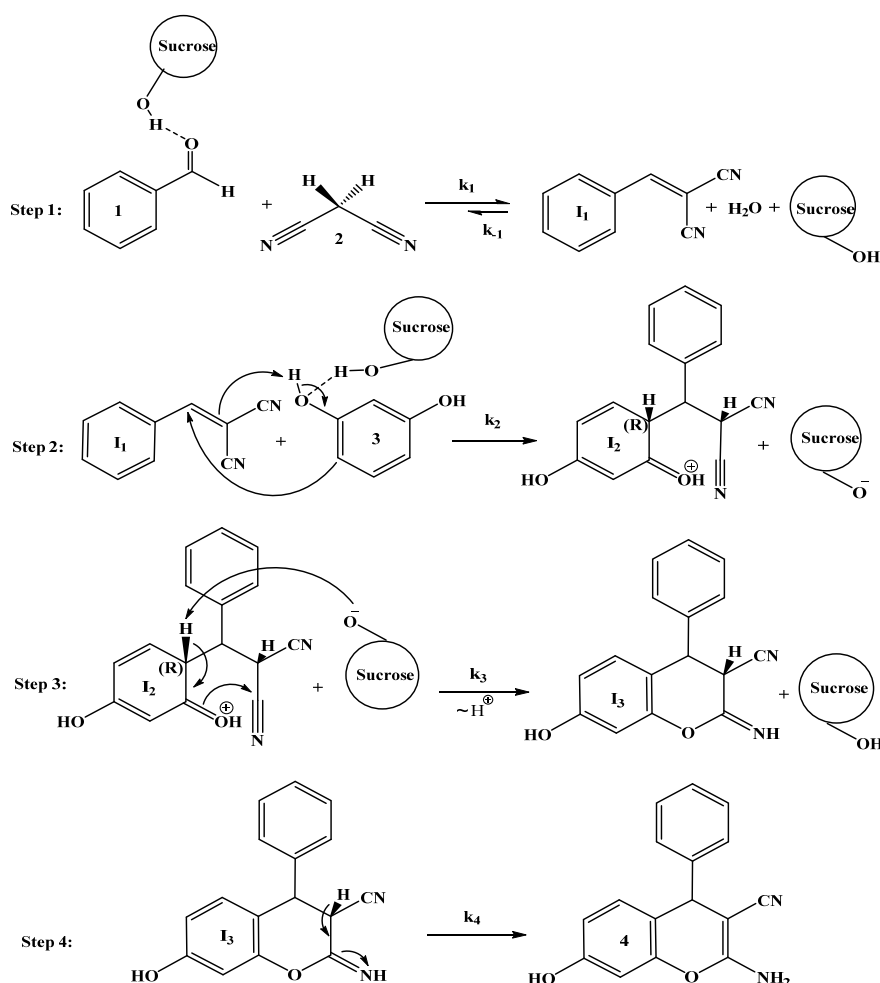
Scheme 2. A simplified scheme of the proposed reaction mechanism

The final equation (15) obtained from the steady state assumption and the mechanism of the reaction is agreement with the experimental equation (3a) and indicates that the overall order of the reaction is two. In addition, in relation to this equation, the partial order with respect to each reactant 1, 2 and 3 is one, one and zero, respectively. Because of the presence of k_1 in the rate low (equation (15)), it obvious that first step (k_1) is a rate determining step (*RDS*) and k_2 should be a fast step. In the other hand, because the transition state (step 1, Scheme 2) in reaction carries a dispersed charge, solvents with higher dielectric constant speed up reaction rate by stabilizing the species at the transition state more than reactants, and therefore E_a would be lower (Table 5). The activation parameters which involve $\Delta G^{\ddagger}$, $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ can be now calculated for the first step (*RDS*, k_1), as an elementary reaction, on the basis of Eyring equation (Fig. 4a, equation (16)).

Fig. 4b shows also a different linearized form of Eyring equation (equation (17)) [26]. Statistical analysis of the Eyring equation clearly confirms that the standard errors of $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ correlate (T_{av} is the center of the temperature range used):

$$\sigma(\Delta S^{\ddagger}) = 1/T_{av}\ \sigma(\Delta H^{\ddagger}) \tag{18}$$

It follows that in most solution phase studies $\sigma(\Delta S^{\ddagger}) \approx \sigma(\Delta H^{\ddagger}) \times 0.0034\ \mathrm{K}^{-1}$. This correlation has been mentioned elsewhere [26,27]. The standard errors for activation parameters have been calculated according to above instructions [26-28] and they have been reported along with these parameters in Fig. 4. With respect to the values of $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ (Fig. 4b), the value of $\Delta G^{\ddagger}$ for the reactions between 1, 2, 3 and sucrose in a mixture of water and ethanol (3:1), and 298 K is 41 kJ mol^{-1}.

3.3.2. Effect of solvent and temperature

In order to determine the effect of temperature and solvent environment on the reaction rate, previous experiments were repeated under different temperatures and solvents. For this purpose, a mixture of ethanol and water (water/ethanol, 3:1) and another mixture of ethanol and water (water/ethanol, 9:1) have been used in the experiment. The results showed that rate of reaction speeds up in solvent with high dielectric constant (water/ethanol, 9:1) with respect to lower dielectric constant (water/ethanol, 3:1) at all temperatures (Table 5). As can be seen in Table 5, the rate of reaction increases in each solvent at higher temperatures. In the studied temperature range, the second-order rate constant (lnk_1) of the reaction was inversely proportional to the temperature, which is agreement with the Arrhenius equation. This behavior is shown in Fig. 5. The activation energy, for the reaction between 1, 2, 3 and sucrose was obtained in a mixture of water and ethanol (9:1) (E_a=102±0.46 kJ/mol) form the slope of Fig. 5.

4. Conclusions

The overall order of reaction for the formation of 2-amino-4*H*-chromene in the presence of sucrose followed second-order kinetics and the partial orders with respect to benzaldehyde 1, malononitrile 2 and resorcinol 3 were one, one and zero, respectively. The results showed that rate of reaction speeds up in solvent with high dielectric constant (water/ethanol, 9:1) with respect to lower dielectric constant (water/ethanol, 3:1) at all temperatures. In the studied temperature range, the second-order rate constant of the reaction was inversely proportional to the temperature, which was agreement with the Arrhenius equation. The first step of proposed

Table 5. Rate constants k_{obs} (M^{-1}min^{-1}) and k_1 (M^{-2}min^{-1}) for the reaction between 1 (5×10^{-4} M), 2 (5×10^{-4}M) and 3 (5×10^{-4} M) and sucrose (10^{-4} M) in different solvent media and temperatures.

Solvent: mix of water/ethanol (3:1) (66.1)[a]					
T	T = 279.2 K	T = 284.2 K	T = 289.2 K	T = 294.2 K	T = 299.2 K
k_1	2.122 (0.0008)[b]	3.525 (0.0009)	12.073 (0.0008)	21.834 (0.0028)	26.9 (0.0030)
k_{obs}[c]	2.1×10^4	3.5×10^4	12×10^4	22×10^4	27×10^4
Solvent: mix of water/ethanol (9:1) (74.3)[a]					
T	T = 6 °C	T = 11 °C	T = 16 °C	T = 21 °C	T = 26 °C
k_1	2.312 (0.0008)[b]	4.261 (0.0011)	12.357 (0.0009)	27.828 (0.0012)	35.374 (0.0041)
k_{obs}[c]	2.3×10^4	4.3×10^4	12×10^4	28×10^4	35×10^4
$ln\ (k_1/T)$	4.417	5.010	6.057	6.852	7.075
$T \times ln\ (k_1/T)$	1233	1424	1752	2016	2117

[a]Dielectric constant (D)
[b]Standard deviation (SD).
[c]$k_{obs} = k_1$[Cat]

$$\ln\left(\frac{k_1}{T}\right) = \left(\ln\frac{k_B}{h} + \frac{\Delta S^{\ddagger}}{R}\right) - \frac{\Delta H^{\ddagger}}{RT} \quad (16)$$

$$\Delta S^{\ddagger} = 196 \pm 1.5 \;{}^{J}\!/_{mol}$$

$$\Delta H^{\ddagger} = 100 \pm 0.461 \;{}^{kJ}\!/_{mol}$$

$$T \times \ln\left(\frac{k_1}{T}\right) = T \times \left(\ln\frac{k_B}{h} + \frac{\Delta S^{\ddagger}}{R}\right) - \frac{\Delta H^{\ddagger}}{R} \quad (17)$$

$$\Delta S^{\ddagger} = 195 \pm 1.5 \;{}^{J}\!/_{mol}$$

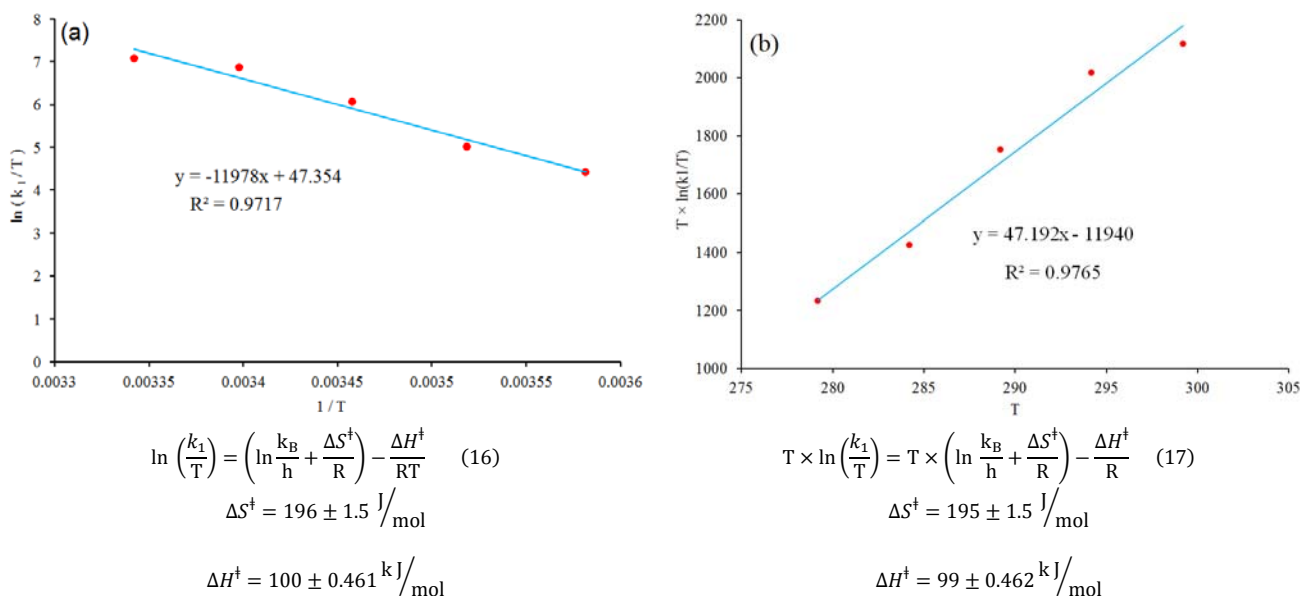$$\Delta H^{\ddagger} = 99 \pm 0.462 \;{}^{kJ}\!/_{mol}$$

Fig. 4. Eyring plots according to equations (16 and 17), for the reaction between **1**, **2**, **3** and sucrose in a mixture of water and ethanol (9:1).

mechanism was recognized as a rate-determining step (k_1) and this was confirmed based upon the steady-state approximation. It was observed that yield was the function of temperature, since the yield increased as the reaction temperature rose, at 85°C , the product was obtained in an excellent yield and at the higher temperature did not increase the reaction yield. Moreover, 20 mol% was chosen as a suitable amount of catalyst for this reaction.
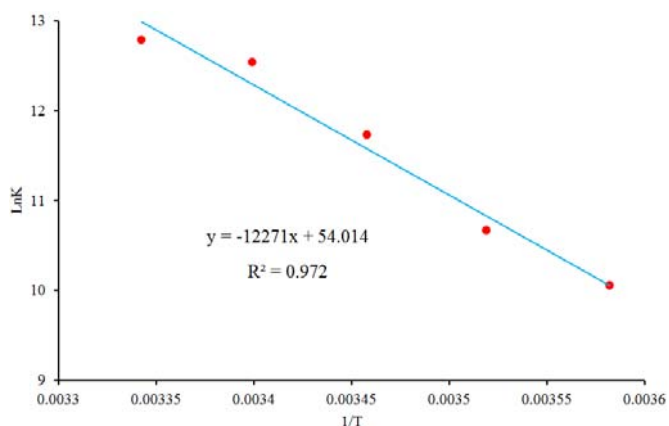
Acknowledgement

Fig. 5. The Dependence of the second order rate constant (ln k_1) on reciprocal temperature for the reaction between compounds 1, 2, 3 and sucrose measured in a mixture of ethanol and water (9:1) at wavelength of 340 nm.

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