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Kinetics and a mechanistic aspect of the reaction between 4-bromobenzaldehyde and 2-aminobenzamide in the presence of formic acid as a solvent: Catalyzed by TBAB and trichloroacetic acid

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Abstract: In recent work, kinetic and a mechanistic study were performed for the reaction between 4-bromobenzaldehyde **1** and 2-aminobenzamide **2** in the presence of formic acid as a solvent, catalyzed by TBAB and Trichloroacetic acid. UV/vis spectrophotometery technique is employed to investigate the kinetics parameters and mechanism of the reaction. The second order fits were automatically drawn, and the values of the second order rate constants (k_2) were automatically calculated using standard equations. The second-order rate constant dependency on the temperature was in agreement with the Arrhenius and Eyring equations. Furthermore, useful information was obtained from studies of the effect of solvent, concentration and catalyst of reagents on the reaction rate. The results showed that the first step of 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: Mechanism, Kinetics, Catalyst, 4-bromobenzaldehyde, 2-aminobenzamide.

Introduction

Heterocyclic chemistry comprises at least half of all organic chemistry research worldwide. In particular, heterocyclic structures form the basis of many pharmaceutical, agrochemical and veterinary products. 4(3H)-Quinazolinones and related quinazolines are classes of fused heterocycles that are of considerable interest because of the diverse range of their biological properties, for example, anticancer, diuretic, anti-inflammatory, anticonvulsant and antihypertensive activities[1-4]. Moreover, several of these compounds used as kinase inhibitors [5] such as gefitinib, erlotinib, caneratinib, dacomitinib, afatinib, vandetanib, ispinesib. Some quinazoline derivatives interact with tubulin [6] and interfere with its polymerization, others act by modulating aurora kinase activity [7] or have an effect in critical phases in the cell cycle [8] or act as apoptosis inducers [9]. Usefulness of multi component reaction can be rationalized by multiple advantages of MCRs over traditional multistep sequential simply mixing the assembly of target compounds. In MCRs, a molecule is assembled in one convergent chemical step in one pot by corresponding starting materials as opposed to traditional ways of synthesizing a target molecule over multiple sequential steps. At the same time, considerably complex molecules can be assembled by MCRs. This has considerable advantages as it saves precious time and drastically reduces effort [10-11]. Formic acid is a good solvent for heterocyclic compounds, as a convenient hydrogen donor for catalytic transfer hydrogenation, Unfortunately, so far the use of these attractive green alternatives requires high-temperature and/or pressure operations, which make the laboratory-scale synthesis difficult, Formic

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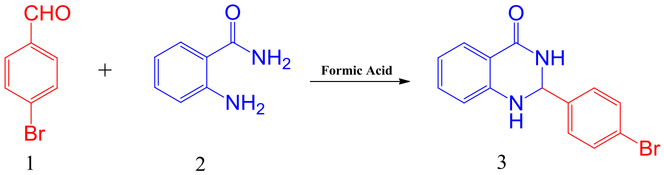
*Corresponding author. Tel: (+98) 54 33446565, Fax: (+98) 54 33446565, E-mail: smhabibi@chem.usb.ac.ir acid (FA) is one of the major products formed in biomass processing and also easily accessible by hydrolysis of methyl formate or by CO2 hydrogenation [12-13]. In the past decade, a variety of synthetic methods have been employed for the preparation of functionalized quinazoline and quinazolinone motifs such as 2,3-dihydroquinazolin-4(1H)-ones and the level of interest in the current domain is clearly shown by the number of publications reporting an extremely high output of results as well as the presence of these scaffolds in numerous marketed medicines as core structures [14] that most general ones involves cyclocondensation of anthranilamides with aldehydes in the presence of various promoting agents, such as Sc(OTf)3 [15], p-toluenesulfonic acid / DDQ[16], I2 /KI in water [17], CuCl2 in ethanol [18] and KMnO4 under microwave irradiation [19]. Other methods such as cyclocondensation of 2-aminobenzamides with substituted benzoyl chlorides [20], one-pot reaction of isatoic anhydride, ammonium acetate and aldehydes using Ga (OTf) 3 [21] or I2 under solvent-free conditions [22] are also reported for the synthesis of these compounds. We present a novel mild, green approach, efficient and economically method for the synthesis of 2, 3-dihydroquinazolin-4(1H)-ones by the reaction of 2-aminobenzamide with benzaldehyde in the presence of formic acid as a catalyst and solvent at room temperature (Scheme **1**).

The aim of the present paper is describe experimental studies of the kinetics and mechanisms of the reactions between 4-bromobenzaldehyde and 2-aminobenzamid. In our previous work, experimental and theoretical kinetics studies and mechanism investigation have fully been discussed for various reactions [23-31]. 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.



1 2 3

Scheme 1: The two-component reaction between 4-bromobenzaldehyde **1** and 2-aminobenzamide **2** in the presence of formic acid.

Results and discussion

Kinetics:

For the kinetic study of the reaction between 4-bromobenzaldehyde **1** and 2-aminobenzamide **2** in the presence of formic acid as a solvent (Scheme **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 each compound **1, 2** were prepared in formic acid as solvent and catalyst. The relevant spectrum of each compound was recorded at the wavelength range between 200 to 500 nm. Figures **1** *and* **2** exhibit the ultraviolet spectra of compounds **1** and **2** respectively.

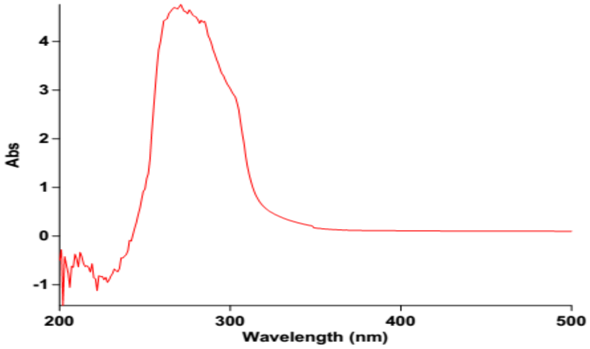


Figure 1: The UV spectrum of 2×10^{-2} M 4-bromobenzaldehyde **1** in formic acid.

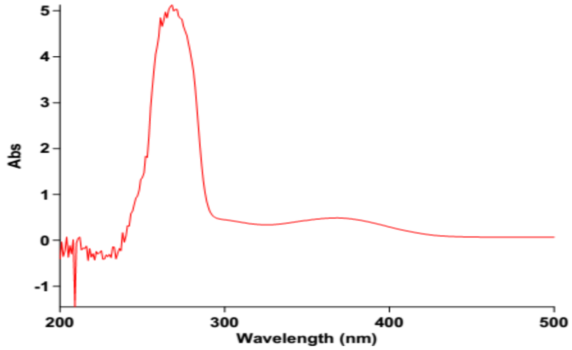


Figure 2: The UV spectrum of 2×10^{-2} M 2-amino-benzamide **2** in formic acid.

In the second experiment, the reaction mixture was started into a 10 mm quartz spectrophotometer cell with 2× 10^{-2} M solution of each compound **1** and **2**, along with formic acid according to stoichiometry of each compound in the overall reaction. The reaction was monitored by conducting scans of the entire spectrum with 3 minutes intervals during the whole reaction time at ambient temperature **(**Figure **3).** From this, the appropriate wavelengths were discovered to be 410 and 420 nm**.** Since at these wavelengths, reactants **1**, **2** and formic acid have no relatively absorbance value, 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 compound product was measured over the concentration range (10^{-3} M ≤ M product ≤10^{-2} M) to confirm a linear relationship between the absorbance and concentrations values.

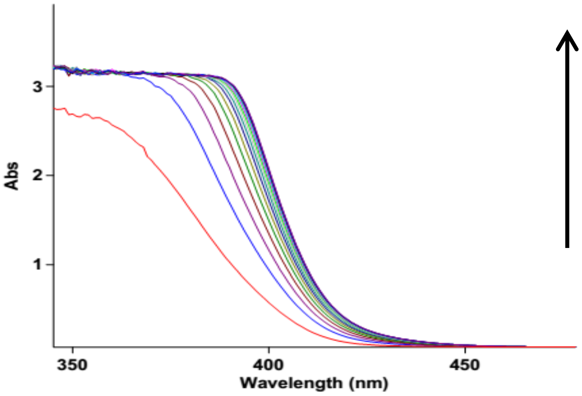


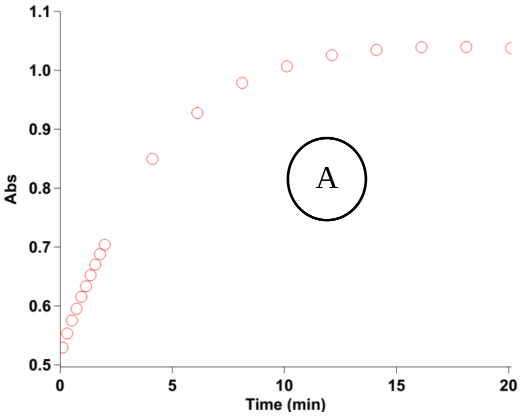
Figure 3: Absorption changes versus wavelength for the reaction between 4-bromobenzaldehyde **1** 10^{-2} M and 2-aminobenzamide **2** 10^{-2} M in the presence of formic acid.

Herein, the upward of direction of the arrow indicate that the progress of product versus times.

In the third experiment under same condition with the previous experiment the absorbance curve was recorded versus time at 25℃ and 410 and 420 nm. This is shown in Figure **4-A** (dotted line) which exactly fits to second order experimental curve (solid line), Figure **4-B**. The second-order rate constant is then automatically calculated using the standard equations within the program at 25°C [35]. It is obvious that the reaction is the second order**.** In this case, overall order of rate law can be written as: α+β= 2

Experimental rate low

(1) Rate = k_{ovr} [1][2]



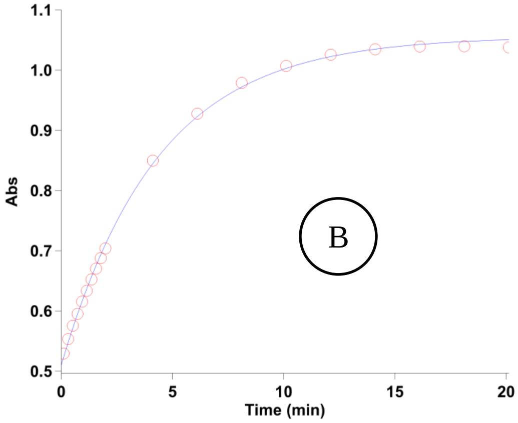


Figure 4: A. The original experimental absorbance curve versus time (dotted line) **B.** second pseudo order fit curve (solid line) accompanied by the original experimental curve (dotted line) for the reaction between **1** 10^{-2} M and **2** 10^{-2} M in the presence of formic acid.

Effects of concentration:

In order to find the partial order of reactants under pseudo-order condition, in a separate experiment (fourth experiment), a same procedure was employed with this concentrations [(10^{-3} M, reactant **1**) and (10^{-2} M, reactant **2**)]. For obtaining equations (2), the rate law can be expressed:

$$\text{Rate} = k_{ovr} [1]^{\alpha} [2]^{\beta}$$

$$\text{Rate} = k_{obs} [1]^{\alpha}$$

$$k_{obs} = k_{ovr} [2]^{\beta} \quad (2)$$

The infinity absorbance (A_{∞}), is the absorbance at reaction completion, obtain able from Figure **6** at t = 20 min**.** With respect to this value, the zero, first or second curve fittings can be drawn automatically for the reaction using the software [35] associated with the UV-Vis instrument**.** The original experimental absorbance against time data made a pseudo-second-order available fit curve at 420 nm, which exactly fits the experimental curve (dotted line) displayed in Figure **5.** Herein, observation rate constant (k_{obs}) was automatically calculated for the equation (2) by the software associated within the UV-vis instrument**.** As a result, since α=1, it is reasonable to accept that the reaction is first order with respect to compound **2** (β =1). Because the overall order of reaction is 2 (α+β=2).

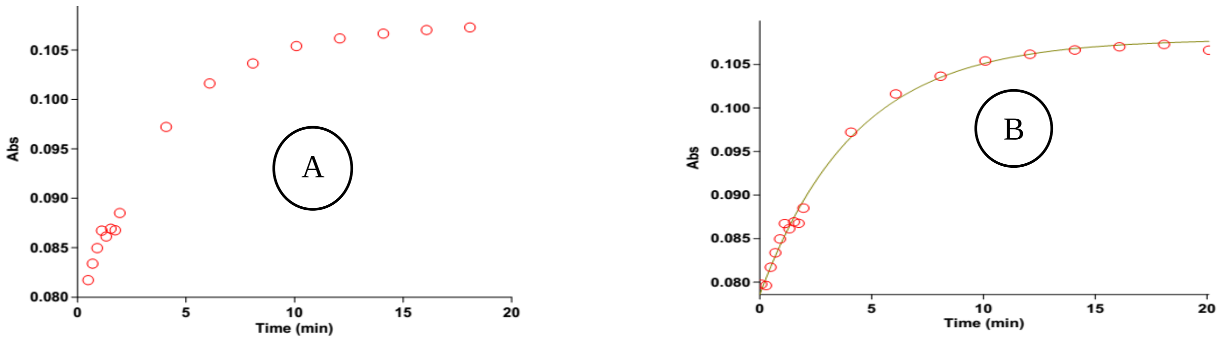


Figure 5: A. The original experimental absorbance curve versus time (dotted line) **B.** first pseudo order fit curve (solid line) for the reaction between **1** (10^{-3} M) and **2** (10^{-2} M in formic acid.

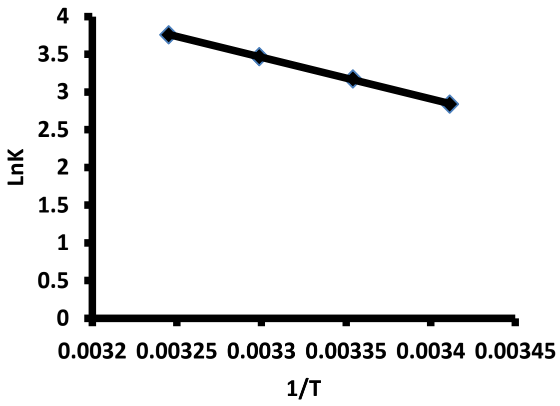
Effect of solvents and temperature:

To determine the effect of changes in temperature and the solvent environment on the rate of reaction, it was elected to perform various experiments under different temperatures and solvent polarities, but otherwise, under the same conditions as for the previous experiment. All the experiments were repeated at different temperatures, including 20, 25, 30 and 35 °C. For each reaction obtained the second-order rate constants of reaction. The reaction at 20 °C needs more time to complete the reaction as compared with other 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 20 to 35°C. To finding the solvent effect, lone formic acid and a mixture of formic acid / acetic acid (7:3) have been used in the experiment, The results showed that rate of reaction speeds up in solvent with high dielectric constant (formic acid) in comparison with lower dielectric constant (mixture of formic acid/ acetic acid (7:3) at all temperatures (Table **1**). Rate constant (k_{ovr}) of the reaction was inversely proportional to the temperature according to the Arrhenius equation (3)

$$\ln k = \ln A - \frac{E_a}{RT} \qquad (3)$$

Rate constants for the reaction at the different temperatures for the reaction between **1** and **2** were obtained in formic acid and a mixture of formic acid / acetic acid (7:3) were plotted against 1/T and the activation energy (*E*a) was calculated from the slope of the Arrhenius plot (as shown in Figure **6**) which shows a good straight line with the slope of –Ea/R as in the equation (3).

$$\ln k = \ln A - \frac{E_a}{RT} \qquad (3)$$



Ea= 45.849 +- 0.008 kj/mol

Figure 6: Dependence of second order ($\ln k_{\mathrm{ove}} = \ln k_2$) on reciprocal temperature for the reaction between reactants **1** and **2** in the presence of formic acid at wavelength 420 nm in accordance with Arrhenius equation.

On the basis of Eyring equation (4):

$$\ln\frac{k}{T} = -\frac{\Delta H^{\ddagger}}{RT} + \frac{\Delta S^{\ddagger}}{R} + \ln\frac{k_B}{h} \qquad (4)$$

That k_B = Boltzmann's constant, T = temperature, h = Planck's constant and R = universal gas constant

Figure **7-A** was plotted and kinetic parameters were estimated. The activation parameters $\Delta H^{\ddagger}$ (activation enthalpy), $\Delta S^{\ddagger}$ (activation entropy) and $\Delta G^{\ddagger}$ (activation Gibbs energy) were determined using the intercept and slope, respectively. Obtained activation parameters in formic acid solvent are given in Figure **7-A** and Table **1.**

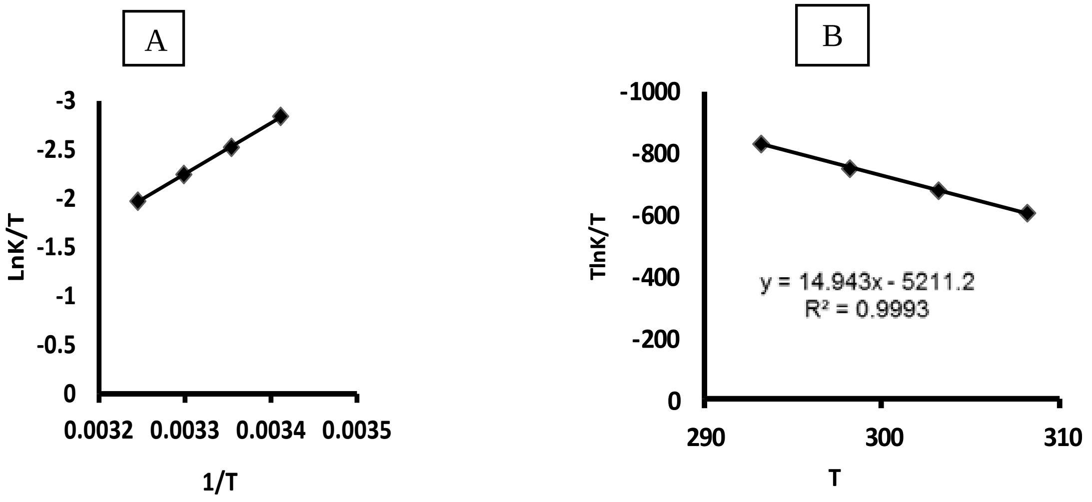
Also, a different linearized form of Eyring equation (T ln (k_{ovr}/T) versus T) [35] were examined (Figure **7-B**) to compare the results obtained from the two methods (Table **1**):

$$T\ln\frac{k}{T} = -\frac{\Delta H^{\ddagger}}{R} + T\left(\frac{\Delta S^{\ddagger}}{R} + \ln\frac{k_B}{h}\right) \qquad (5)$$

The highest activation energy (E_a = 45.8492 kJ. mol^{-1}) was obtained in formic acid, which means the reactants need high energy for transition state, while for a mixture of formic acid / acetic acid (7:3) solvent was smaller that means easier reaction will occur **.**The positive value of $\Delta H^{\ddagger}$ are 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 [36]**.** If $\Delta S^{\ddagger}$ is large and negative, indicates a transition state that is more highly ordered than the reactants **.**The Gibbs free energy was determined using the Equation (6):

$$\Delta G^{\ddagger}=\Delta H^{\ddagger}+T\Delta S^{\ddagger} \qquad (6)$$

The highest activation Gibbs energy was for a mixture of formic acid / acetic acid solvent that means the reaction will occur harder**.**



$$\Delta S^{\ddagger} = -73.22 \pm 0.026\ {}^{J}/_{mol} \qquad \Delta S^{\ddagger} = -73.30 \pm 0.026\ {}^{J}/_{mol}$$

$$\Delta H^{\ddagger} = 43.35 \pm 0.008\ {}^{kJ}/_{mol} \qquad \Delta H^{\ddagger} = 43.32 \pm 0.008\ {}^{kJ}/_{mol}$$

Figure 7-A and **B.** Eyring plots according to equations 16 and 17 for the reaction between **1** and **2** in formic acid.

Table 1: Activation parameters involving $\Delta S^{\ddagger}$, $\Delta H^{\ddagger}$, $\Delta G^{\ddagger}$ and E_a along with Ea in accord with the two methods.

solvent	$\Delta H^{\ddagger}$ (kJ.mol^{-1})	$\Delta S^{\ddagger}$ (J.mol^{-1}K^{-1})	$\Delta G^{\ddagger}$ (kJ.mol^{-1})	Ea (kJ.mol^{-1})
formic acid	43.35	-73.22	65.18	45.85
formic acid/acetic acid (7:3)	49.96	-55.39	66.48	52.46

Table 2: Values of the overall rate constants for the reaction between **1** and **2** in the presence of different solvents at all temperatures investigated at 420 and 410 nm.

(λ) (nm)	Solvent	20.0 ºC	25.0 ºC	30.0 ºC	35.0 ºC
420	Formic acid	17.097	23.877	32.07	42.85
410	Formic acid	16.56	22.683	32.939	42.985
420	Aceticacid/formic acid (1:4**)**	9.6295	14.101	21.08	30.85
410	aceticacid/formic acid (1:4**)**	10.67	13.765	20.85	30.75

Effect of catalyst:

Tetrabutylammonium bromide (TBAB) can be used as a cationic ionic liquid catalyst. Recently tetrabutylammonium bromide (TBAB) has been used as an extremely useful homogeneous catalyst in various organic transformations [16–18]. TBAB is a readily available with inherent properties like environmental compatibility, nonflammability, operational simplicity, noncorrosive nature, ease of reusability and excellent thermal and chemical stability. It is therefore of interest to examine the behavior of TBAB as catalyst in the synthesis of quinazolinone derivatives. Our knowledge is relevant to cyclocondensation of 2-aminobenzamide with aromatic aldehydes for the synthesis of 2-aryl-2,3-dihydroquinazolin-4(1H)-ones and 2-arylquinazolin-4(3H)-ones.In this work, rate of reaction was increased in the presence of TBAB and Trichloro acetic acid as a second and third catalyst in comparison with the first catalyst formic acid. (Table **2**). TBAB and trichloro acetic acid speeds up slightly the rate of reaction.

Table 3: Effect of various catalysts on a reaction between **1**(10^{-2} M) and **2** (10^{-2} M) compounds in the presence of formic acid solvent.

		k_{ove}($min^{-1}.M^{-2}$)
(λ) (nm)	Catalyst	25.0 ºC
420	Formic acid	23.877
410	Formic acid	22.683
420	TBAB	26.213
410	TBAB	28.457
420	Trichloro acetic acid	25.371
410	Trichloro acetic acid	28.312

Speculative Mechanism:

Utilizing the above results, the simplified scheme of the proposed reaction mechanism Figure **8** is shown in Figure **9**.

To investigate which steps of the proposed mechanism could be rate determining step (RDS), the rate law is written using the final step for the product 3:

$$rate = k_4[I_3]$$

(7)

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

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

(8)

$$k_3[I_2] = k_4[I_3]$$

(9)

The value of equation 9 can be replaced in the equation 7 so the rate equation becomes:

$$rate = k_3[I_2]$$

(10)

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

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

(11)

$$k_3[I_2] \qquad = k_2[I_1]$$

(12)

The value of equation 12 can be replaced in the equation 10 so the rate equation becomes:

$$rate = k_2[I_1]$$

(13)

For obtaining the concentration of intermediate $[I_1]$ the following equations yielded by applying the steady state assumption:

$$\frac{d[I_1]}{dt} = k_1[1][2][cat] - k_2[I_1] = 0$$

(14)

$$k_1[1][2][cat] = k_2[I_1]$$

(15)

The value of equation 15 can be replaced in the equation 13 so the rate equation becomes:

$$rate = k_1[1][2][cat]$$

(16)

$$k_{ove} = k1[Cat]$$

(17)

$$Rate = kove[1][2]$$

(18)

The final equation 14 indicates that the overall order of the reaction is two which was formerly confirmed by the experimental data equation 1. Because of the presence of K_1 in the rate low (18), it obvious that first step (K_1) is a rate determining step.

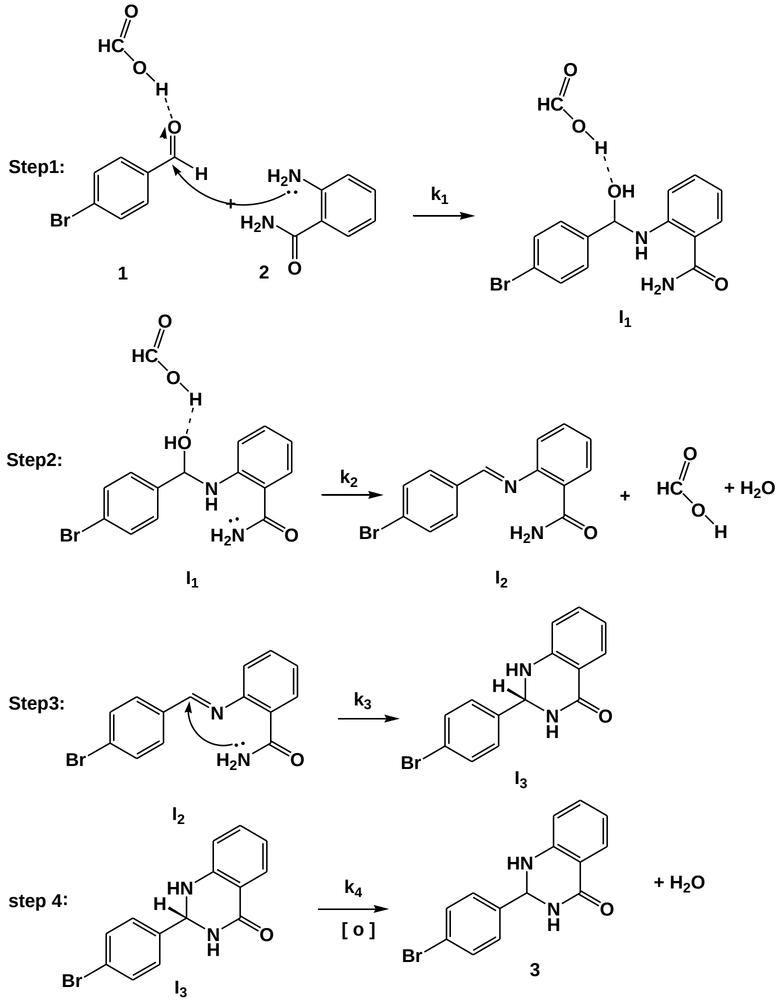


Figure 8: Proposed mechanism for the reaction between 4-bromobenzaldehyde **1** and 2-aminobenzamid **2** in the presence of formic acid as a solvent.

$$\text{step 1:} \quad 1 + 2 + \text{cat} \xrightarrow{k_1} I_1$$

$$\text{step 2:} \quad I_1 \xrightarrow{k_2} I_2 + \text{cat} + H_2O$$

$$\text{step 3:} \quad I_2 \xrightarrow{k_3} I_3$$

$$\text{step 4:} \quad I_3 \xrightarrow[\text{[o]}]{k_4} 3 \quad + H_2O$$

Figure 9: The simplified Scheme for the proposed reaction between 4-bromobenzaldehyde **1** and 2-aminobenzamide **2** in the presence of formic acid.

Conclusion

Kinetic investigation of recent reaction was undertaken using UV spectrophotometry technique. The results can be summarized as follow:

1) The overall reaction order followed second order kinetics and the reaction orders with respect to each of the reactant 2-aminobenzaldehyde 1 and 4-boromobenzaldehide 2 compounds is one and one.

2) With respect to the experimental data, the first step of proposed mechanism was recognized as a rate-determining step (k_1).

3) in a solvent with higher dielectric constant the rate of reaction increased. This can be pertained to different stabilizing effects of solvent on reactants and activated complex.

4) These data provided the suitable plots for calculating the activation energy (Ea = 45.849 ± 0.008) and parameters ($\Delta S^{\neq}$ = -73.22 , $\Delta H^{\neq}$ = 43.35 and $\Delta G^{\neq}$= 65.18) of the reaction.

(5) The values of Ea and $\Delta H^{\neq}$ in present work speeded up the rate of reaction.

(6) Positive values of $\Delta S^{\neq}$ (less negative values) cause the reaction proceed fast.

(7) Positive values of $\Delta G^{\neq}$ imply that reaction is rot spontaneous.

Experimental

Chemicals and Apparatus:

The 4-bromobenzaldehyde **2** and 2-aminobenzamide **1** were obtained from Merck (Darmstadt, Germany), Acros (Geel, Belgium) and Fluka (Buchs, Switzerland), and used without further purifications**.** All extra pure solvent including the formic acid and mixture of acetic acid / formic acid (1:4) 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**.**

Synthesis of 2, 3-dihydro-2-phenylquinazolin-4(1H)-one:

The mixture of 2-aminobenzamide (1 mmol), benzaldehyde (1 mmol), and formic acid (1 cm^3) were stirred at room temperature.The progress of the reaction is monitored by TLC (ethyl acetate: petroleum ether 3:1). The reaction mixture was poured into 10 cm^3 ice water. On solidification, it was filtered, washed with ice water, and recrystallized from ethanol to give the pure 2, 3-dihydro-2-phenylquinazolin-4(1H)-one.

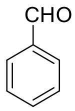
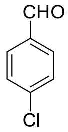
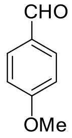
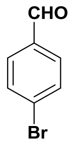
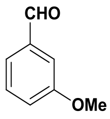
In addition, the same model reaction was carried out in formic acid at different temperatures to access the effect of temperature to the reaction yield. At 30˚C, the product was obtained in an excellent yield and at the higher temperature did not increase the reaction yield.(Table **4**).

The mentioned procedure was employed for the synthesis of 2, 3-dihydro-2-phenylquinazolin-4(1H)-one derivatives using formic acid (Table **5**).

Table 4: Optimization of temperature in synthesis of 2,3-dihydro-2-phenylquinazolin-4(1H)-one by using formic acid (1 ml).

Entry	°C (Temperature)	Yield (%)
1	25	87
2	30	98
3	40	96
4	50	89
5	60	78
6	70	70

Table 5: Synthesis of 2, 3-dihydro-2-phenylquinazolin-4 (1H)-one derivatives using formic acid.

Entry	Derivatives	Product	Time (h)	Yield (%)	MP(Obsd)(°C)	MP(Lit)(°C)
1		a	2	98	222-223	221-222[32]
2		b	1.5	99	308-309	305-307[33]
3		c	3	53	247-249	248-249[34]
4		d	1.5	98	313-315	315-316[33]
5		e	3	84	202-205	209-211[33]

Acknowledgement

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