RSC Advances

PAPER

View Article Online
View Journal | View Issue

Cite this: *RSC Adv.*, 2015, **5**, 52508

Effect of different substituents on the one-pot formation of 3,4,5-substituted furan-2(5*H*)-ones: a kinetics and mechanism study†

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Received 23rd May 2015
Accepted 9th June 2015

DOI: 10.1039/c5ra09717g

www.rsc.org/advances

The kinetics of reactions between benzaldehyde and diethyl acetylenedicarboxylate with *para*-substituted anilines for the one-pot formation of 3,4,5-substituted furan-2(5*H*)-ones have been studied spectrally at different temperatures in formic acid. For all substituents at the *para* position of the aniline ring, the reaction followed second-order kinetics. The partial orders with respect to substituted aniline and diethyl acetylenedicarboxylate were one and one, and the reactions also revealed zero-order kinetics in relation to benzaldehyde. *Para*-electron donating substituents on the aniline ring increased the rate of reaction. On the basis of experimental data, a three step mechanism has been proposed. Kinetic values (k and E_a) and associated activation parameters ($\Delta H^{\neq}$, $\Delta G^{\neq}$ and $\Delta S^{\neq}$) of the reactions were determined.

1. Introduction

A multicomponent reaction (MCR) is a process in which three or more accessible components combine to produce a final product that displays the features of all inputs and thus offers greater possibilities for molecular diversity per step with a minimum of synthetic time and effort in a single reaction.

Synthesis of furan-2(5*H*)-ones as subunits in a large number of natural products[1–5] is a *significant* target for organic and medicinal chemists. Highly substituted furans are a structural component of a vast number of biologically active natural and synthetic compounds such as anticancer,[6,7] anti-inflammatory,[8] antifungal,[9,10] antimicrobial,[11,12] and antiviral HIV-1.[13–15] The reactions leading to the formation of furanones are frequently reported by several research groups, however, they have proposed the reactions mechanism without offering evidence to support them.[16–20] There are a number of reasons for tendency to know reaction mechanisms. Knowledge of mechanisms aids the synthetic chemist in predicting by products and improving reaction conditions, the most powerful tool for the experimental study of reaction mechanisms is chemical kinetics. Kinetics is the study of the speed with which a chemical reaction occurs, and with all of the factors which influence these rates.[21]

The spectroscopic technique is the largest and important techniques used in chemistry. The most widely method used for kinetic and mechanistic studies of chemical reactions is ultraviolet-visible (UV-visible) spectroscopy. Several research studies have documented over a large area of different reactions which have previously been reported using the UV-visible spectrophotometry technique.[22–30] In our previous work, experimental and theoretical kinetics studies and mechanism investigation have fully been discussed for various reactions.[31–37] In continuing our investigations on the kinetic of the organic reactions, we focused on 3,4,5-substituted furan-2(5*H*)-ones by one-pot multicomponent reaction that was reported by MT Maghsoodlou and coworkers.[38] Depending upon the stoichiometry and conditions, other products have also been reported for this reaction.[39–42] However, under optimized conditions reported by M. T. Maghsoodlou and *et al.* (Fig. 1),[38] 3,4,5-substituted furan-2(5*H*)-ones are obtained in high ylides

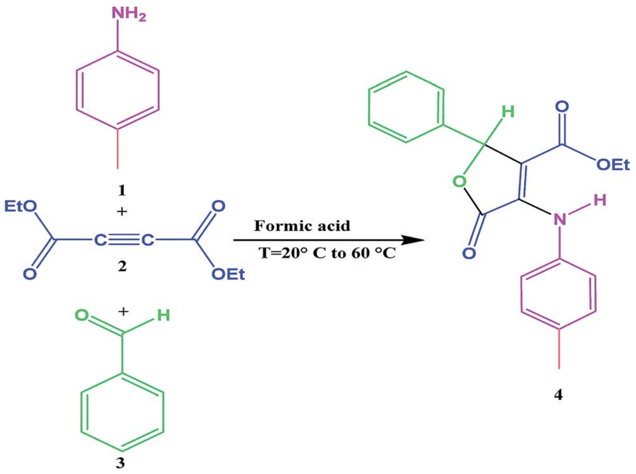

Fig. 1 The three-component synthesis of furan-2(5*H*)-ones.[38]

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c5ra09717g

(%90–98). In the current work for the first time, we describe kinetic results together with the detailed mechanistic studies for the mentioned reactions based on a global kinetic analysis methodology using the UV-vis spectrophotometry apparatus. Also, this work focused especially on the effects of temperature, different *para*-substituted anilines on the activation parameters of preparation reaction of 3,4,5-substituted furan-2(5*H*)-ones.

2. Experimental

2.1. Chemicals and apparatus used

All chemicals were used without further purification. Substituted-aniline **1**, diethyl acetylenedicarboxylate **2** and benzaldehyde **3** were supplied by Merck (Darmstadt, Germany), Acros (Geel, Belgium) and Fluka (Buchs, Switzerland). Extra pure formic acid and acetic acid were also obtained from Merck (Darmstadt, Germany).

A Cary UV-vis spectrophotometer model Bio-300 with a 10 mm light-path quartz spectrophotometer cell equipped with thermostated housing cell was used to record absorption spectra in order to follow reaction kinetics.

2.2. General procedure

The first experiment is performed with 10^{-2} M solutions of aniline **1**, diethyl acetylenedicarboxylate **2** and benzaldehyde **3** in formic acid solvent. The progress of reaction is monitored by the absorbance changes as a function of wavelengths (Fig. 2). Since at wavelength of 420 nm, reactants **1**, **2** and **3** have no relatively absorbance values, it provides the opportunity to fully investigate the kinetics and mechanism of the reaction. Hence, the product absorbance changes with time are undertaken under the same condition at wavelength of 420 nm (Fig. 3) at 20 °C. As can be seen in Fig. 3, the original experimental absorbance curve *versus* time (dotted line) is exactly fitted to second order fit curve (solid line). So the reaction is second order ($\alpha + \beta + \gamma = 2$), the overall reaction rate is described by the kinetic equation:

$$\text{Rate} = k_{\text{ovr}}[\mathbf{1}]^{\gamma}[\mathbf{2}]^{\beta}[\mathbf{3}]^{\alpha} \tag{1}$$

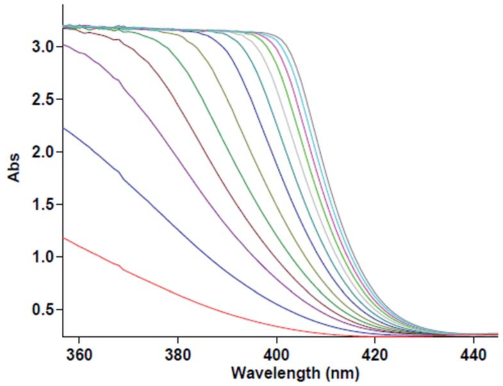

Fig. 2 Absorption changes *versus* wavelength for the reaction between **1** (10^{-2} M), **2** (10^{-2} M) and **3** (10^{-2} M) in formic acid for generation of product **4**.

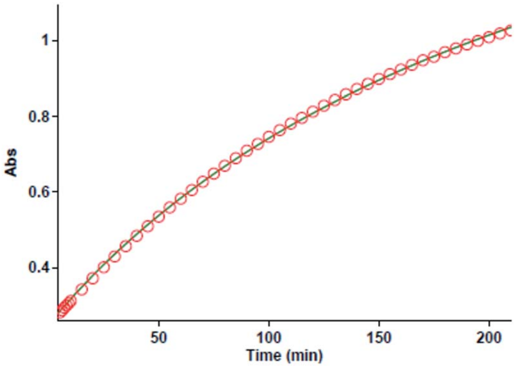

Fig. 3 The original experimental absorbance curve *versus* time at selected wavelength of 420 nm for the reaction between **1** (10^{-2} M) and **2** (10^{-2} M) with **3** (10^{-2} M) in formic acid. Dotted line is experimental values and the solid line is a fit curve.

Then the second-order rate constant ($k_{\text{ovr}} = 3.50\ \text{min}^{-1}\ \text{M}^{-2}$) is automatically calculated using the standard equations within the program at 20 °C.[34]

3. Results and discussion

3.1. Effects of concentration

In order to obtain partial order with respect to aniline **1**, pseudo-order condition is performed for the reaction. So **in the second experiment**, we followed the reaction kinetics by plotting the UV-vis absorbance *versus* time at wavelength of 420 nm with **1** (10^{-3} M), **2** (10^{-2} M) and **3** (10^{-2} M) at 20.0 °C in formic acid. For this case the rate law can be expressed:

$$\text{Rate} = k_{\text{ovr}}[\mathbf{1}]^{\alpha}[\mathbf{2}]^{\beta}[\mathbf{3}]^{\gamma}$$

$$\text{Rate} = k_{\text{obs}}[\mathbf{3}]^{\gamma} \tag{2}$$

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

All kinetic mathematical fits (the zero, first or second fit curve) are done using the software[43] associated with the UV-Vis spectrophotometer instrument. The original experimental absorbance against time data make a pseudo-first-order available fit curve at 420 nm, which exactly fits the experimental curve, Fig. 4A. Herein, observation rate constant (k_{obs}) is automatically calculated for the eqn (2) by the software associated within the UV-vis instrument. It is obviously that the reaction is of the first order type with respect to aniline **1** ($\alpha = 1$).

Also, to gain the partial order of reaction with respect to reactant **3**, **third experiment** is done under pseudo-order condition [(10^{-2} M, **1**), [(10^{-2} M, **2**) and [(10^{-3} M, **3**)]. In this experiment the original experimental absorbance *versus* time provides a second-order curve ($k_{\text{ovr}} = 3.49\ \text{min}^{-1}\ \text{M}^{-2}$, Fig. 4B) like the first experiment. Due to the concentration changes of

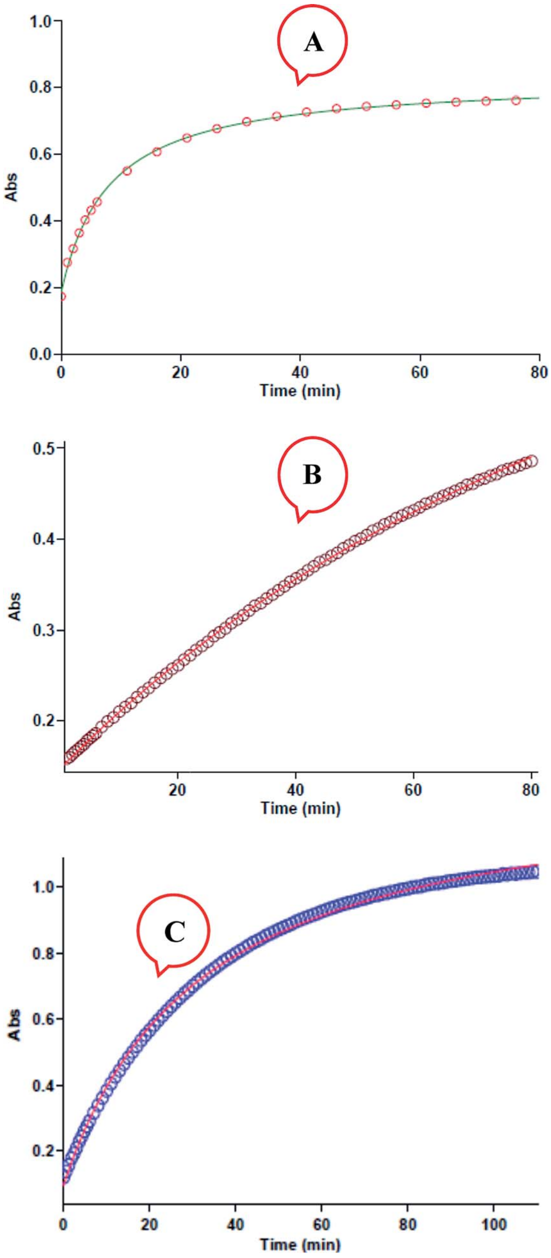

Fig. 4 (A) Plot of absorbance *versus* time at 420 nm for the reaction between **1** (10^{-2} M), **2** (10^{-2} M) and **3** (10^{-3} M) in formic acid. Dotted line is experimental values, and the solid line is fit curve. (B) Plot of absorbance *versus* time at 420 nm for the reaction between **1** (10^{-3} M), **2** (10^{-2} M) and **3** (10^{-2} M) in formic acid. Dotted line is experimental values, and the solid line is fit curve. (C) Plot of absorbance *versus* time at 420 nm for the reaction between **1** (10^{-2} mol L^{-1}), **2** (10^{-3} mol L^{-1}) and **3** (10^{-2} mol L^{-1}) in formic acid, dotted line is experimental values, and the solid line is fit curve.

reactant **3** had no effect on the reaction rate, then reaction is zero-order with respect to reactant **3** ($\gamma = 0$). Also, in **fourth experiment**, we followed kinetics under pseudo order condition of reactant **2**. As can be seen in Fig. 4C, the reaction shows first order kinetics that it means the partial order with respect to reactant **2** is one ($\beta = 1$). So, the reaction between aniline **1** and diethyl acetylenedicarboxylate **2** with benzaldehyde **3** follows second-order kinetics.

According to the obtained results from the four experiments, the rate law of reaction can be written:

$$\text{From the first experiment: } \alpha + \beta + \gamma = 2$$

$$\text{From the second experiment: } \alpha = 1$$

$$\text{From the third experiment: } \alpha + \beta = 2 \text{ and } \gamma = 0$$

$$\text{From the fourth experiment: } \beta = 1$$

$$\text{Rate} = k_{\text{ovr}}[\mathbf{1}][\mathbf{2}]$$

3.2. Effect of solvents and temperature

The solvent dielectric constant and polarity are important parameters that influence rate constants. Solvent effects on the rate of reaction depend on the relative stabilization of the starting materials and the corresponding transition state through solvation.[44,45] For investigation of the effect of medium dielectric constant on the rate of reaction, the same kinetic procedure is followed in the presence of acetic acid in 20 °C.

It is found that as medium dielectric constant decreased, the reaction rate reduced from formic acid ($k_{\text{ovr}} = 3.50$ min^{-1} M^{-2}) to acetic acid ($k_{\text{ovr}} = 0.713$ min^{-1} M^{-2}).

Temperature is considered a major factor that affects the rate of a chemical reaction. The influences of temperature on the reaction rate were studied in the range of 20 °C to 60 °C with 10 °C intervals for each reaction and the values of second-order rate constants are determined. Kinetic data are shown in Table 1. Reaction rate constant has a temperature dependency, which is usually given by the Arrhenius equation.

Most reactions are found to obey the Arrhenius equation:

$$k = A\exp\left(\frac{-E_\text{a}}{RT}\right) \tag{3}$$

Taking the natural logarithm of both sides of the equation provides:

$$\ln k = \ln A - \frac{E_\text{a}}{RT} \tag{4}$$

where E_a is the activation energy of reaction, R is universal gas constant (8.314 J K^{-1} mol^{-1}), and A is frequency factor.

The activation energy of reaction is usually determined experimentally by plotting the graph of ln k *versus* the reciprocal of the temperature $1/T$, which will yield a straight line with a slope of $-\frac{E_\text{a}}{RT}$ and an intercept ln A (Fig. 5). The highest activation energy ($E_\text{a} = 80.12$ kJ mol^{-1}) is obtained for NO_2-aniline, that means reaction will occur slower than alone aniline and *para*-donating substituent-aniline. Nevertheless, the differences in activation energies are not much, because the substituents on aniline ring are far from the center of reaction. The Eyring equation is used in chemical kinetics to describe the variance of the rate of a chemical reaction with temperature and was used

Table 1 Reaction rate constant (k_{ovr} (min^{-1} M^{-2})) in different temperatures and different substituted-aniline under the same conditions for the reaction between **1** (10^{-2} M) and **2** (10^{-2} M) with **3** (10^{-2} M) in formic acid

(λ) (nm)	Substituted-aniline	20.0 °C	30.0 °C	40.0 °C	50.0 °C	60.0 °C
420	OMe-aniline	8.10 (0.0028)[a]	24.31 (0.0057)	52.53 (0.0063)	115.42 (0.0023)	210.31 (0.0039)
420	Ethyl-aniline	6.16 (0.0026)	15.9 (0.0068)	34.88 (0.0074)	91.97 (0.0064)	174.10 (0.0075)
420	Aniline	3.50 (0.0046)	9.06 (0.0038)	20.40 (0.0038)	48.45 (0.0025)	115.35 (0.0037)
420	F-aniline	0.75 (0.0029)	2.10 (0.0057)	5.12 (0.0037)	12.87 (0.0010)	32.938 (0.0037)
420	NO_2-aniline	0.44 (0.0022)	1.40 (0.0029)	3.42 (0.0026)	9.33 (0.0021)	23.84 (0.0072)

[a] Standard deviation (SD).

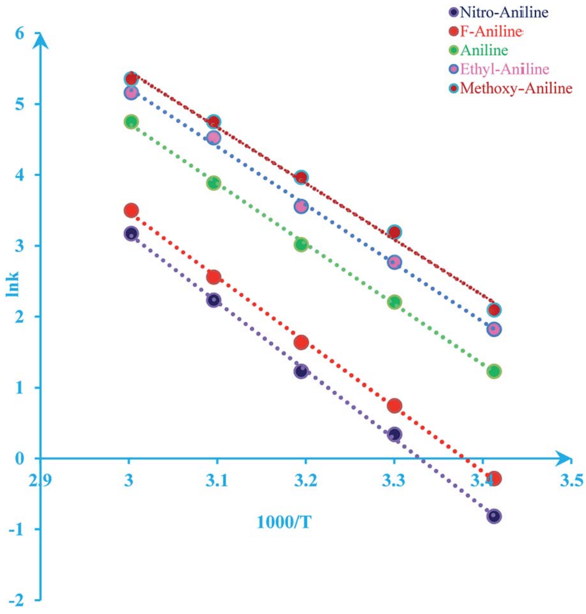

Fig. 5 Dependence of second order (ln k_{ovr} = ln k_1) on reciprocal temperature for the reaction between reactants **1**, **2** and **3** in formic acid measured at wavelength 420 nm in accordance with Arrhenius equation.

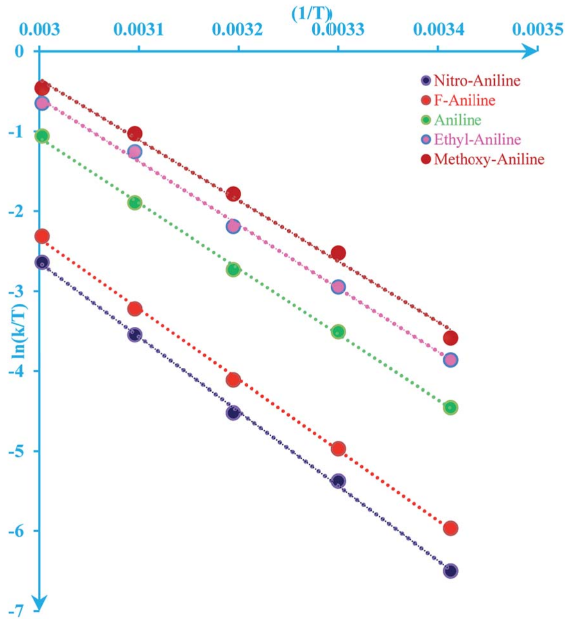

Fig. 6 Eyring plot (ln $\frac{k_{ovr}}{T}$ *versus* *T*) according to eqn (5) for the reaction between **1**, **2** and **3** in formic acid.

to evaluate activation parameters involving $\Delta H^{\neq}$ (activation enthalpy), $\Delta S^{\neq}$ (activation entropy).[46]

The linear form of the Eyring equation is given below:

$$\ln\frac{k}{T} = -\frac{\Delta H^{\neq}}{RT} + \frac{\Delta S^{\neq}}{R} + \ln\frac{k_B}{h} \tag{5}$$

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

The values for $\Delta H^{\neq}$ (activation enthalpy), $\Delta S^{\neq}$ (activation entropy) can be determined from slopes and intercepts of ln $\frac{k}{T}$ *versus* 1/*T* plot (Fig. 6). Obtained activation parameters for *para*-substituted aniline are given in Tables 2 and 3.

Also, the transition state equation was used to calculate activation parameters $\Delta H^{\neq}$, $\Delta S^{\neq}$ in order to check the results obtained from the two methods (Eyring and the transition state theory). According to the transition state theory, activation energy can be related to activation enthalpy (eqn (6)) and also

Table 2 Activation parameters ($\Delta S^{\neq}$, $\Delta H^{\neq}$, $\Delta G^{\neq}$ and E_a) using the Arrhenius eqn (3) and Eyring eqn (5) and (6) in 20 °C

Substituted-aniline	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (J mol^{-1} K^{-1})	$\Delta G^{\neq}$ (kJ mol^{-1})	E_a (kJ mol^{-1})
OMe-aniline	63.08	−11.20	59.24	65.67
Ethyl-aniline	65.91	−4.67	64.92	68.51
Aniline	68.17	−2.01	68.76	70.76
F-aniline	73.46	3.40	74.83	76.05
NO_2-aniline	77.53	13.10	80.81	80.12

Table 3 Activation parameters ($\Delta S^{\neq}$, $\Delta H^{\neq}$, $\Delta G^{\neq}$ and ln *A*) using the Arrhenius eqn (3) and The transition state eqn (6)–(8) in 20 °C

Substituted-aniline	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (J mol^{-1} K^{-1})	$\Delta G^{\neq}$ (kJ mol^{-1})	ln *A*
OMe-aniline	60.71	−18.87	66.34	29.15
Ethyl-aniline	63.55	−12.36	67.24	29.94
Aniline	65.80	−9.68	68.69	30.26
F-aniline	71.09	−4.27	72.37	30.91
NO_2-aniline	75.16	5.42	73.55	32.08

pre-exponential factor is relevant to activation entropy according to eqn (8) and (9), respectively:[46]

$$E_a = \Delta H^{\neq} + 2RT \tag{6}$$

$$A = \frac{ek_BT}{h} e^{\frac{\Delta S^{\neq}}{R}+2} \tag{7}$$

$$\Delta S^{\neq} = R\left(\ln A - \ln\left(\frac{e^2k_BT}{h}\right)\right) \tag{8}$$

The values obtained on the basis of transition state theory inferred that the activation enthalpy is the lowest for donating substituent-aniline that have the higher reaction rates and the highest for withdrawing substituent-aniline with the lowest reaction rates (Table 3). Note that the negative activation entropy indicated a greater degree of ordering in the transition state than in the initial state. These results suggest that the transition state in first step of reaction, Fig. 8, involving donating substituent-aniline is ordered more effectively stabilized than the transition state containing withdrawing substituent-aniline (Tables 2 and 3). The activation Gibbs free energy has also been evaluated from the following form of the Gibbs–Helmholtz equation:

$$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq} \tag{9}$$

The activation free energy is essentially the energy requirement to get a molecule (or a mole of them) to undergo the reaction. It is of interest to note that activation free energies $\Delta G^{\neq}$ for the different substituents are positive. The value of the activation free energy for donating substituent-aniline is lower than withdrawing substituent-aniline that means the reaction will occur harder for withdrawing substituent-aniline.

To investigate the impact of the different substituents on the rate constant of reaction and activation parameters, we changed the substituents R on aniline from the electron donating (methoxy, ethyl) to the electron withdrawing (fluorine, nitro) group. The reaction provides respective Schiff base and is reversible in absence of reactant **3**. The first step of reaction consists of Michael addition. According to the experimental observations, the first step is slow (please see Mechanism section 3.3). Then, electron donating groups cause the aniline more nucleophilic and accelerate the reaction.

3.3. Mechanism

In separate experiments, reactions between aniline **1** and diethyl acetylenedicarboxylate **2** (Re. (1)), aniline **1** and benzaldehyde **3** (Re. (2)), and then diethyl acetylenedicarboxylate **2** and benzaldehyde **3** (Re. (3)) are performed under the same concentration of each reactant (10^{-2} M) at 20 °C. The Re. (1) is monitored by recording scans of the entire spectra with 5 min intervals in 45 min reaction time at 20 °C (Fig. 7A). The Re. (2) was monitored by recording scans of the entire spectra with 1 min intervals during the whole reaction time (5 min) at 20 °C (Fig. 7B). There are no reactions between reactants **2** and **3** due to the lack of any progress. Moreover, some ^{1}HNMR information about the reaction products is presented in ESI file,† and also the about first intermediate $\mathbf{I_1}$ was reported previously.[47,48] According to these references, the first step of the reaction consists of Michael addition and is slow which respective diethyl 2-aryloamino-fumarate $\mathbf{I_1}$ can be readily synthesize and characterized according to known protocols and can be purified by convenient distillation, then, $\mathbf{I_1}$ can be used for subsequent steps.[49,50] As a result of these preliminary investigations and experimental observations, the speculative mechanism containing three steps with starting reaction between reactants **1** and **2** (the more rapidly occurring reaction amongst competing reactions) is proposed in Fig. 8.

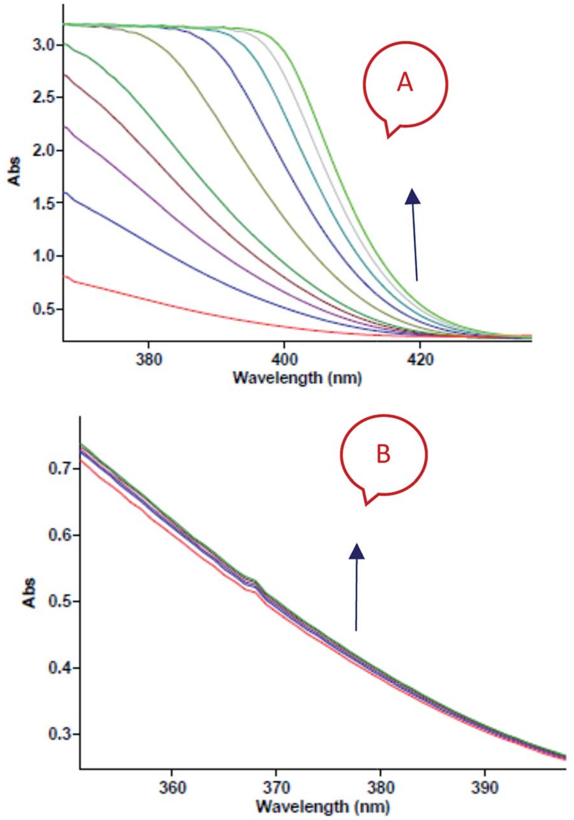

Fig. 7 (A) Changes in absorption spectra *vs.* wavelength in 20 °C for the reaction between aniline **1** and diethyl acetylenedicarboxylate **2** in formic acid as reaction proceeds into a 10 mm light-path cell. The total acquisition time was 45 min; the time increment was set to 5 min. Herein, the upward of direction of the arrow indicate that the progress of reaction. (B) Changes in absorption spectra *vs.* wavelength in 20 °C for the reaction between aniline **1** and benzaldehyde **3** in formic acid as reaction proceeds into a 10 mm light-path cell. The total acquisition time was 5 min; the time increment was set to 1 min. Herein, the upward of direction of the arrow indicate that the progress of reaction.

For the reaction, a steady state treatment is coupled with the kinetic observations. So, the rate law is written using the final step of the proposed mechanism in Fig. 8 for the generation of product **4**:

$$\text{Rate} = k_5[\mathbf{I_4}] \tag{10}$$

Also, the overall reaction can be written as:

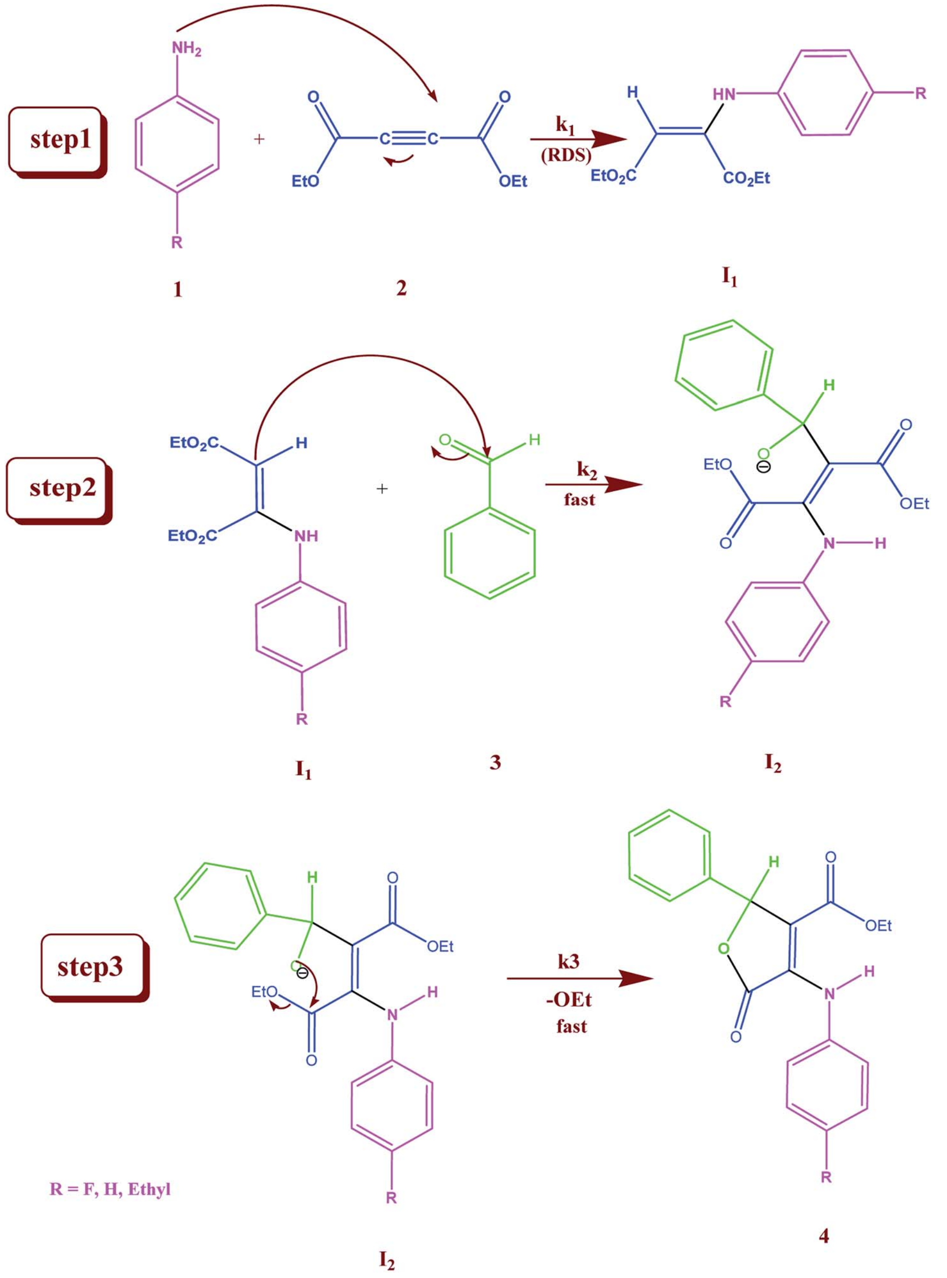

Fig. 8 Speculative mechanism for the reaction between aniline **1** and diethyl acetylenedicarboxylate **2** with *para*-substituted benzaldehyde **3** for generation of product **4** in formic acid.

$$\text{Rate} = k_1[\mathbf{1}][\mathbf{2}] \tag{11}$$

This makes it possible to accept that the first step is the rate-determining step (RDS) of the reaction and the overall order of reaction is two since k_1 is the only rate constant which appeared in the eqn (11). This equation, obtained from the proposed mechanism, is same with the rate law that resulted from UV-vis experiment (rate = k_{ovr} [**1**][**2**]). It is possible to analyze the effect of the solvent on the reaction, because the first step (k_1) is the rate determining step, in this case in both solvents the transition state partially charged, in solvent with higher dielectric constant the transition state is highly solvated relative to the reactant molecules that have no any charge.

If the second step to be a rate determining step, therefore, the first step is fast with forward rate constant (k_1) and return rate constant (k_{-1}). We can write the rate law:

$$\text{Rate} = k_2[\mathbf{I_1}][\mathbf{3}],\quad \frac{\mathrm{d}[\mathbf{I_1}]}{\mathrm{d}t} = k_1[\mathbf{1}][\mathbf{2}] - k_{-1}[\mathbf{I_1}] - k_2[\mathbf{I_1}][\mathbf{3}] = 0 \tag{12}$$

$$[\mathbf{I_1}] = \frac{k_1[\mathbf{1}][\mathbf{2}]}{k_2[\mathbf{3}] + k_{-1}} \tag{13}$$

$$\text{Rate} = \frac{k_2 k_1[\mathbf{1}][\mathbf{2}][\mathbf{3}]}{k_2[\mathbf{3}] + k_{-1}} \tag{14}$$

According to the above assumption, k_2 is a rate determining step, therefore it is logical to express $k_{-1} \gg k_2[\mathbf{3}]$.

As a result, rate law becomes:

$$\text{Rate} = \frac{k_2 k_1[\mathbf{1}][\mathbf{2}][\mathbf{3}]}{k_{-1}} \tag{15}$$

herein, the overall order of recent rate law is three and is not compatible with the rate law arising from UV-vis experiment (rate = $k_{\text{ovr}}[\mathbf{1}][\mathbf{2}]$), so the second step could not be a rate determining step.

4. Conclusions

Kinetics and mechanism of the reactions between *para*-substituted anilines **1** and diethyl acetylenedicarboxylate **2** with benzaldehyde **3** were investigated in formic acid and the below results were obtained:

A mechanism involving three steps was proposed for the reactions. The overall order of reaction followed second-order kinetics and the partial orders with respect to *para*-substituted aniline, diethyl acetylenedicarboxylate and benzaldehyde were one, one and zero, respectively. Also, the first step of the reaction is recognized as a rate-limiting step according to the experimental data. The electron donating group on substituted aniline more stabilized the transition state than the electron withdrawing group and with decreasing the activation energy the value of rate constant (k_1) was speed up. The rate of reaction was also accelerated by increasing the temperature and was in agreement with Arrhenius, Eyring equations and the transition state equations.

Acknowledgements

We gratefully acknowledge financial support from the Research Council of the University of Sistan and Baluchestan.

References

1 N. B. Carter, A. E. Nadany and J. B. Sweeney, *J. Chem. Soc., Perkin Trans. 1*, 2002, 2324.

2 Q. H. Chen, P. N. Praveen and E. E. Knaus, *Bioorg. Med. Chem.*, 2006, **14**, 7898.

3 J. Boukouvalas, S. Cote and B. Ndzi, *Tetrahedron Lett.*, 2007, **48**, 105.

4 A. Zarghi, P. N. Praveen and E. E. Knaus, *Bioorg. Med. Chem.*, 2007, **15**, 1056.

5 M. Braun, A. Hohmann, J. Rahematpura, C. Buhne and S. Grimme, *Chem.–Eur. J.*, 2004, **10**, 4584.

6 F. Bellina, E. Falchi and R. Rossi, *Tetrahedron*, 2003, **59**, 9091.

7 S. Takahashi, A. Kubota and T. Nakata, *Tetrahedron Lett.*, 2002, **43**, 8661.

8 S. Padakanti, M. Pal and K. R. Yeleswarapu, *Tetrahedron*, 2003, **59**, 7915.

9 S. M. Hein, J. B. Gloer, B. Koster and D. J. Malloch, *Nat. Prod.*, 2001, **64**, 809.

10 M. Pour, M. Spulak, V. Balsanek, J. Kunes, P. Kubanova and V. Butcha, *Bioorg. Med. Chem.*, 2003, **11**, 2843.

11 L. M. Levy, G. M. Cabrera, J. E. Wright and A. M. Seldes, *Phytochemistry*, 2003, **62**, 239.

12 G. Grossmann, M. Poncioni, M. Bornand, B. Jolivet, M. Neuburger and U. Sequin, *Tetrahedron*, 2003, **59**, 3237.

13 S. Hanessian, R. Y. Park and R. Y. Yang, *Synlett*, 1997, **4**, 351.

14 S. Hanessian, R. Y. Park and R. Y. Yang, *Synlett*, 1997, **4**, 353.

15 A. Choudhury, F. Jin, D. Wang, Z. Wang, G. Xu, D. Nguyen, J. Castoro, M. E. Pierce and P. N. Confalone, *Tetrahedron Lett.*, 2003, **44**, 247.

16 N. Hazeri, M. T. Maghsoodlou, N. Mahmoudabadi, R. Doostmohammadi and S. Salahi, *Curr. Organocatal.*, 2014, **1**, 45–50.

17 R. Doostmohammadi, M. T. Maghsoodlou, N. Hazeri and S. M. Habibi-Khorassani, *Res. Chem. Intermed.*, 2013, **39**, 4061.

18 R. Doostmohammadi and N. Hazeri, *Lett. Org. Chem.*, 2013, **10**, 199.

19 M. S. Narayana, *et al.*, *Tetrahedron*, 2009, **65**, 5251.

20 R. M. Mohammad, *et al.*, *C. R. Chim.*, 2014, **17**, 131.

21 F. A. Carey and R. J. Sundberg, *Advanced Organic Chemistry, Part A*, Structure Mechanisms Kluwer Academic Press, New York, 2000.

22 O. J. Nielsen, J. Sehested, S. Langer, E. Ljungström and I. Wängberg, *Chem. Phys. Lett.*, 1995, **238**, 359.

23 V. V. Ivanov and C. Decker, *Polym. Int.*, 2001, **50**, 113.

24 M. C. Almandoz, Y. A. Dávila, M. I. Sancho, E. I. Gasull and S. E. Blanco, *Spectrochim. Acta, Part A*, 2010, **77**, 51.

25 L. L. Lu, Y. H. Li and X. Y. Lu, *Spectrochim. Acta, Part A*, 2009, **74**, 829.

26 J. J. C. Erasmus, M. M. Conradie and J. Conradie, *React. Kinet., Mech. Catal.*, 2012, **105**, 233.

27 B. P. Kalyan and K. S. Gupta, *Transition Met. Chem.*, 2012, **37**, 671.

28 A. K. Chandra, *J. Mol. Model.*, 2012, **18**, 4239.

29 L. Sandhiya, P. Kolandaivel and K. Senthilkumar, *Struct. Chem.*, 2012, **23**, 1475.

30 M. Pandeeswaran and K. P. Elango, *J. Solution Chem.*, 2009, **38**, 1558.

31 S. M. Habibi Khorassani, A. Ebrahimi, M. T. Maghsoodlou, M. Shahraki and D. Price, *Analyst*, 2011, **136**, 1713.

32 M. Dehdab, S. M. Habibi-Khorassani and M. Shahraki, *Catal. Lett.*, 2014, **144**, 1790.

33 S. M. Habibi-Khorassani, M. T. Maghsoodlou, E. Aghdaei and M. Shahraki, *Prog. React. Kinet. Mech.*, 2012, **37**, 301.

34 M. Shaharaki, S. M. Habibi-Khorassani, A. Ebrahimi, M. T. Maghsoodlou and A. Paknahad, *Prog. React. Kinet. Mech.*, 2012, **37**, 321.

35 M. Shahraki and S. M. Habibi-Khorassani, *J. Phys. Org. Chem.*, 2015, **28**, 396.

36 S. M. Habibi-Khorassani, A. Ebrahimi, M. T. Maghsoodlou, O. Asheri, M. Shahraki, N. Akbarzadeh and Y. Ghalandarzehi, *Int. J. Chem. Kinet.*, 2013, **45**, 596.

37 S. S. Pourpanah, S. M. Habibi-Khorassani and M. Shahraki, *Chin. J. Catal.*, 2015, **36**, 757.

38 R. Doostmohammadi, M. T. Maghsoodlou and S. M. Habibi-Khorassani, *Iran J. Org. Chem.*, 2012, **4**, 939.

39 L. Longyun, *et al.*, *ACS Comb. Sci.*, 2013, **15**, 183.

40 R. Sarkar and C. Mukhopadhyay, *Tetrahedron Lett.*, 2013, **54**, 3706.

41 M. Zhang and J. Huan-Feng, *Eur. J. Org. Chem.*, 2008, **20**, 3519.

42 M. Zhang, *et al.*, *Synlett*, 2007, **20**, 3214.

43 O. J. Nielsen, J. Sehested, S. Langer, E. Ljungström and I. Wängberg, *Chem. Phys. Lett.*, 1995, **238**, 359.

44 C. Lerveny and V. Ruzicka, *Adv. Catal.*, 1981, **30**, 335.

45 M. Mortimer and P. Taylor, *Chemical Kinetics and Mechanism*, The Royal Society of Chemistry, Thomas Graham House, Science Park, Milton Road, Cambridge, CB4 OWF, UK, 2002.

46 K. J. Laidler, *Theories of Chemical Reaction Rates*, McGraw-Hill, New York, 1941.

47 M. M. Mashaly, S. R. El-Gogary and T. R. Kosbar, *J. Heterocycl. Chem.*, 2014, **51**, 1078.

48 C. Huang, Y. Yin, J. Guo, J. Wang, B. Fan and L. Yang, *RSC Adv.*, 2014, **4**, 10188.

49 J. Safaei-Ghomi, F. Salimi, A. Ramazani, F. Z. Nasrabadi and Y. Ahmadi, *Turk. J. Chem.*, 2012, **36**, 485.

50 G. Domschke, *Inz. Chem.*, 1980, **20**, 16.