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Effect of phenol on the synthesis of benzoxazine

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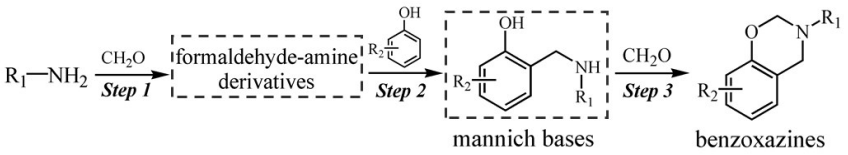
Abstract:
This work aimed to search the key starting materials and the key step of the benzoxazine synthesis using primary amine, phenol and formaldehyde as the starting materials. The reaction kinetics was investigated by gas chromatography. The kinetic parameters of benzoxaznine formation, such as reaction order, rate constants, and activation energy, were found to approximately equal to those of phenol consumption, which revealed that phenol was the key starting material and played an important role in the synthesis of benzoxazine. Furthermore, *step 2,* the reaction between formaldehyde-amine derivatives and phenol for the production of mannich base was the controlling step. This improved insight into the benzoxazine synthesis is expected to help researchers explore novel benzoxazines and control the synthesis of benzoxazines.

Keywords: benzoxazine, phenol, kinetics, key starting materials, key step

1. Introduction

Polybenzoxazine, gained through thermal polymerization of the corresponding 3,4-dihydro-2*H*-3-substituted-1,3-benzoxazine (benzoxazine)[1], has attracted wide extensive interest in scientific and industrial community as it exhibits many excellent properties (for instance, superior molecule design flexibility[2,3], excellent mechanical properties[4,5], good heat resistance[6,7], low dielectric constant[8,9] and near-zero volumetric shrinkage during polymerization[10,11]). Such properties has led to their wide applications in many areas, such as microelectronics and aeronautical technology. These fascinating properties are strongly influenced by benzoxazine, so the study on controlling the synthetic process of benzoxazine is of great interest. To be more specific, understanding which starting materials or intermediates determine the synthesis and which steps control the process, or in other words, searching the key starting materials or intermediates and key steps, are crucial.



Scheme 1 Synthesis of benzoxazine from phenol, primary amine and formaldehyde.

For the synthesis of benzoxazine, the most popular route is using formaldehyde, phenols and primary amines as starting materials[12-14]. In this route, formaldehyde-amine derivatives, e.g., (like *N*-hydroxymethyl amine, *N*,*N*-dihydroxymethyl amine, *N*,*N*'-diphenyl methane diamine, and triazine) are initially generated very fast[15-17](Scheme 1, *step 1*) and then react with phenols to form mannich bases (Scheme 1, *step 2*)[18]. Finally, benzoxazines are formed *via* the dehydration reaction between mannich bases and formaldehyde (Scheme 1, *step 3*)[19,20]. For this route, *N*,*N*-dihydroxymethyl amine or *N*-hydroxymethyl amine which belongs

to the formaldehyde-amine derivatives, are generally considered as the key intermediates[14]. Nevertheless, formaldehyde-amine derivatives are generated very fast, and no clear correlations between the consumption of primary amine (or the formation of formaldehyde-amine derivatives) and the formation of benzoxazine are established. Therefore, formaldehyde-amine derivatives may not be decisive for the formation of benzoxazines, and as a result, *step 1* may not be the key step for controlling the synthesis. Some other work have also attempted to investigate key intermediates. Particularly, the reaction between 2-phenylaminomethylphenol (mannich base) and formaldehyde (Scheme 1, *step 3*) has been studied by our group[21]. It was found that the formation of benzoxazine was rapid and no intermediate 2-(*N*-hydroxymethyl-N-phenylamino)methylphenols were observed. These indicated that mannich base may be a key intermediate in *step 3*, i.e., benzoxazine may be generated quickly while mannich base was formed. Therefore, questions still remain- how to search for the key starting materials or intermediates and what is the controlling step. If the kinetic parameters of benzoxaznine formation approximately equal to those of starting materials, the starting materials are the key starting materials and played an important role in the synthesis of benzoxazine. Furthermore, the starting materials-involving reaction will be the controlling step. In this work, we hence aim to search the key starting materials by probing the kinetics of benzoxazine synthesis. Additionally, we are interested in understanding the controlling step of the synthetic process.

Gas chromatography (GC) is widely used in petrochemical[22,23], pharmaceutical[24,25], environment[26,27] and biochemistry[28,29] due to its advantages such as efficiency, high sensitivity, small sample consumption, and ease of operation. In this work, we employ GC technology to probe the kinetics of benzoxazine synthesis using *n*-propylamine, phenol, and aqueous formaldehyde solution as starting materials at different conditions (i.e., reaction temperature and time). The results indicate that phenol plays an important role and *step 2* (phenol reacts with formaldehyde-amine derivatives to generate mannich bases) is identified as the key step. Detailed analysis and discussions are provided.

2. Experimental section

2.1 Materials

Phenol (≥99%, ACS) was purchased from Aladdin Chemistry Co. Ltd. *N*,*N*-dimethylformamide (≥99.5%, AR), *n*-propylamine (≥99%, AR) 1,4-dioxane (≥99.5%, AR), petroleum ether (≥96%，boiling range 69-90°C，AR), ethyl acetate (≥99.5%, AR), anhydrous calcium chloride (≥96%, AR) and sodium hydroxide (≥96%, AR) were purchased from the Chengdu Kelong Chemical Reagents Corp. Paraformaldehyde (≥98%, CP) was purchased from Ercros Industrial S.A. Spain. Diethyl ether (≥99%, AR) was purchased from the Chengdu Changlian Chemical Reagents Corp. All reagents were used as received.

2.2 Preparation of aqueous formaldehyde solution

The aqueous formaldehyde solution was prepared as follows: 70 g water was adjusted to pH 8 using 4% NaOH solution. Paraformaldehyde (1 mol, 30 g) was added and the mixture was stirred at 70°C for 1 hour to form a transparent solution with pH 5-6. Concentration of formaldehyde was confirmed based on ASTM D2378:2007 and GB/T 9009-2011 using titration with sodium sulfite[21].

2.3 Synthesis of Phenol-*n*-Propylamine-based benzoxazine

1,4-dioxane (15 mL) and 27.73% aqueous formaldehyde solution (0.2 mol, 21.64 g) were introduced into a 100 mL three-necked flask, then, *n*-propylamine (0.1 mol, 5.90 g) was dropwise added while the mixture was stirred at room temperature for 20 minutes. After adding phenol (0.1 mol, 9.40 g) and stirring at 70 °C for 6 h, the solvent was removed using a rotary evaporator to gain the raw products. After that, the raw products were dissolved in 20 mL diethyl ether and washed with 4% NaOH solution and distilled water. After being purified by column chromatography on silica gel using ethyl acetate/petroleum ether mixture (1/12, V/V) as eluent, pale yellow oil was afforded.

3,4-dihydro-2*H*-3-*n*-propyl-1,3-benzoxazine, FTIR (Fig. S1) (KBr, cm^{-1}): 1224 (Ar–O–CH_2), 934 (oxazine ring)[30-32]. ^{1}H NMR (Fig. S2) (400 MHz, DMSO-d6, ppm): d = 6.7–7.1 (4H, Ar–H), 4.81 (s, 2H, O–CH_2–N), 3.92 (s, 2H, N–CH_2–Ar), 2.59（s, 2H, N-CH_2-C）, 1.50 (s, 2H, C-CH_2-C), 0.86 (s, 3H, CH_3). ^{13}C NMR (Fig. S3) (400 MHz, DMSO-d6, ppm): 154.42, 128.14, 127.79, 121.00, 120.53, 116.22, 82.54 (O-CH_2-N), 52.97, 49.67 (Ar-CH_2-N), 21.08, 12.02.

2.4 Reaction of *n*-propylamine, phenol and formaldehyde

Stoichiometric amounts of phenol (0.08 mol, 7.53 g) and 27.73% aqueous formaldehyde solution (0.16 mol, 17.31 g) were dissolved in 1,4-dioxane (50.00 mL) in a 100 mL three-necked flask firstly, then *n*-propylamine (0.08 mol, 4.73 g) was added. In the solution, concentrations of *n*-propylamine, phenol and formaldehyde were 1 mol/kg, 1 mol/kg, and 2 mol/kg, respectively. Afterwards, homogeneous solutions were respectively reacted at 60 °C, 70 °C, 80 °C and 90 °C for a given time. Then 1.0 ± 0.1 g of solution was transferred into a tube and 0.06 g of *N*,*N*-dimethylformamide was added as the internal reference. Afterwards, phenol consumption and benzoxazine formation were measured using GC.

3. Characterization

Fourier transform infrared (FTIR) spectra were obtained on a Nicolet Magna 650 instrument with a resolution of 4 cm^{-1} using KBr films. ^{1}H NMR and ^{13}C NMR spectra were obtained on a Bruker TD-65536 NMR (400MHz) using deuterated dimethyl sulfoxide (DMSO-*d*6) as solvent with tetramethylsilane as internal standard. The quantitative analysis of phenol and benzoxazine was performed by gas chromatography (FILI, GC-9790), with a SE-54 capillary column (30 m × 0.25 mm), a hydrogen flame-ionization detector (FID) and ZB-2020 integrator under the following conditions: injector temperature 270 °C, detector temperature 270 °C, oven temperature 90 °C, carrier gas was nitrogen. *N*,*N*-dimethylformamide was used as an

internal standard.

4. Results and discussion

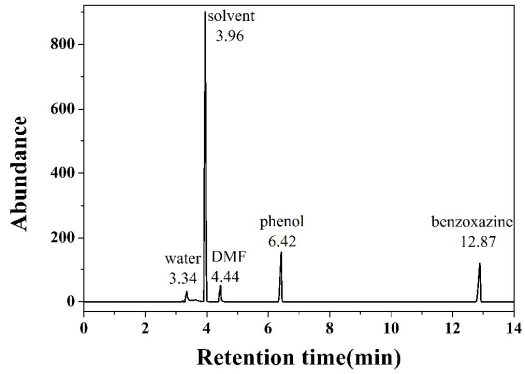


Fig. 1 GC spectrum of the reaction sample of *n*-propylamine, phenol and aqueous formaldehyde at 70 ℃ for 100 minutes.

This work aims to searching key starting materials through probing the kinetics of benzoxazine synthesis by means of studying the reaction kinetics of *n*-propylamine, phenol and formaldehyde in 1,4-dioxane using gas chromatography (GC). The reactions occurred respectively at 60 ℃, 70 ℃, 80 ℃ and 90 ℃, and phenol consumption and benzoxazine formation were detected (Fig. S4). A GC spectrum of the reaction sample at 70 ℃ for 100 min was shown in Fig. 1 as an example. Peaks at 3.34 min, 3.96 min, 4.44 min, 6.42 min and 12.87 min were assigned to water, 1,4-dioxane (solvent), *N*,*N*-dimethylformamide (internal standard, abbreviated as DMF), phenol and benzoxazine, respectively. The concentrations of phenol and benzoxazine can be obtained from the internal standard and calibration factor of GC. Furthermore, the concentrations of phenol and benzoxazine at various reaction temperatures and reaction time can also be gained using this method. Notably, almost no other compounds were observed in the GC spectrum.

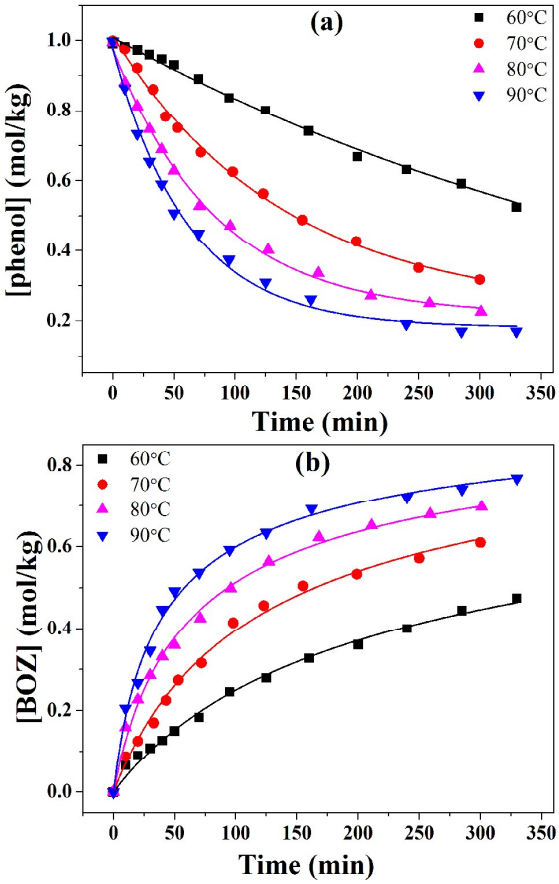
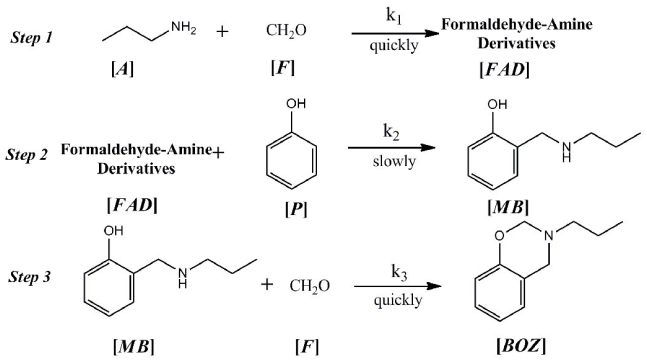


Fig. 2 Reactions of *n*-propylamine, phenol and aqueous formaldehyde at various temperatures. (a) the relationships between phenol concentrations and reaction time, (b) the relationships between benzoxazine concentrations and reaction time.

After obtaining the concentrations of phenol and benzoxazine at various temperatures for different time, relationships between phenol or benzoxazine concentration and reaction time have been established, Fig. 2 (a) and (b). According to Fig. 2 (a), phenol consumption increased as reaction time increased, and the consumption rate also increased with increasing reaction temperature. For the benzoxazine concentration (Fig. 2 (b)), the concentration gradually increased as the reaction time increased, moreover, benzoxazine formation rate also increased with increasing reaction temperature. Interestingly, phenol consumption was approximately equal to benzoxazine formation. For example, after reacting at 60°C for 3 h, 4 h and 5 h, the phenol consumption concentrations were respectively 0.35 mol/kg, 0.43 mol/kg and 0.48 mol/kg, while the sets of the benzoxazine formation concentrations were successively 0.35 mol/kg, 0.40 mol/kg and 0.45 mol/kg. This suggested that almost all the consumed phenol was converted into benzoxazine and little side reactions of phenol occurred. And this also indicated that phenol was possibly the key starting material.



Scheme 2 Reactions in the benzoxazine synthesis from phenol, n-propylamine and formaldehyde.

To prove our hypothesis, we study the kinetic and calculate the parameters of benzoxazine formation and phenol consumption. The kinetic from forming benzoxazine were study primarily. According to the benzoxazine synthesis from phenol, primary amine and formaldehyde, the reaction processes of Phenol-*n* Propylamin-based benzoxazine are illustrated in Scheme 2. Firstly, *n*-propylamine reacts with formaldehyde to form formaldehyde-amine derivatives quickly (Scheme 2, *Step 1*), then formaldehyde-amine derivatives reacts with phenol to form 2-*n*-propylaminomethylphenol (mannich base) (Scheme 2, *Step 2*), benzoxazine is formed finally *via* the dehydration reaction between mannich base and formaldehyde (Scheme 2, *step 3*)[20,21]. In these processes, formaldehyde can be converted into formaldehyde-amine derivatives, mannich base and benzoxazine. Hence, the initial concentration of formaldehyde, $[F]_0$, can be expressed as:

$$[F]_0 = [F] + [FAD] + [MB] + 2[BOZ] \qquad eq\ (1)$$

where $[F]$, $[FAD]$, $[MB]$ and $[BOZ]$ are respectively the concentrations of formaldehyde, formaldehyde-amine derivatives, mannich base and benzoxazine after reacting for a given time.

For formaldehyde-amine derivatives, it can be generated into mannich base and benzoxazine. Therefore, the initial concentration of formaldehyde-amine derivatives $[FAD]_0$ can be expressed as:

$$[FAD]_0 = [FAD] + [MB] + [BOZ] \qquad eq\ (2)$$

Then $[FAD]$ can be obtained from eq (2).

$$[FAD] = [FAD]_0 - [MB] - [BOZ] \qquad eq\ (3)$$

Because the reaction between *n*-propylamine and formaldehyde (Scheme 2, *step 1*) occurs very fast[15-17], the initial concentration of formaldehyde-amine derivatives is approximately equal to the initial concentration of *n*-propylamine ($[A]_0$=1 mol/kg). Then eq (3) becomes:

$$[FAD] = 1 - [MB] - [BOZ] \quad eq\ (4)$$

The initial concentration of formaldehyde $[F]_0$ can be modified from eq (1) as:

$$[F]_0 = [F] + 1 + [BOZ] \quad eq\ (5)$$

Because $[F]_0$=2 mol/kg, eq (5) then can be becomes

$$\frac{d[BOZ]}{dt} = -\frac{d[F]}{dt} \quad eq\ (6)$$

In the case of formation of benzoxazine (Scheme 2, *step 3*), the formaldehyde consumption rate is equal to that of mannich base, then benzoxazine generation rate can be expressed as:

$$\frac{d[BOZ]}{dt} = -\frac{d[F]}{dt} = -\frac{d[MB]_{consume}}{dt} \quad eq\ (7)$$

where $-\frac{d[MB]_{consume}}{dt}$ is mannich base consumption rate at a given time. As reported previously, the reactions between mannich bases and formaldehyde to form benzoxazines are very fast. In other words, once mannich bases are generated, benzoxazines will be generated immediately. Therefore, the benzoxazine formation rate is roughly equal to the mannich base generation rate (Scheme 2, *step 2*). Then eq (7) becomes as follows

$$\frac{d[BOZ]}{dt} = -\frac{d[MB]_{consume}}{dt} = \frac{d[MB]_{generate}}{dt} \quad eq\ (8)$$

where $-\frac{d[MB]_{generate}}{dt}$ is the generation rate of mannich base at a given time. The *step 2* can be expressed as:

$$\frac{d[MB]_{generate}}{dt} = k_2[FAD]^{\alpha_2} \times [P]^{\beta_2} \quad eq\ (9)$$

where [*P*] represents the phenol concentrations at a given time, k_2, α_2 and β_2, relating to *step 2*, respectively denote the reaction rate constant, the reaction order of formaldehyde-amine derivatives and that of phenol. Thus the overall kinetic equation of benzoxazine synthesis can be calculated according to eq (10).

$$\frac{d[BOZ]}{dt} = k_2[FAD]^{\alpha_2} \times [P]^{\beta_2} \qquad eq\ (10)$$

Assuming that k_2, α_2 and β_2 are k, α and β, respectively. eq (10) becomes

$$\frac{d[BOZ]}{dt} = k[FAD]^{\alpha} \times [P]^{\beta} \qquad eq\ (11)$$

where k, α and β, hence corresponding to the whole benzoxazine synthesis process, successively denote the rate constant of benzoxazine synthesis, the overall reaction order of formaldehyde-amine derivatives and that of phenol, respectively. As can be seen from eq (11), interestingly, the overall benzoxazine formation rate is depending on mannich base generation rate.

Because the benzoxazine formation is approximately equal to the phenol consumption as mentioned previously, phenol concentration can be expressed as:

$$[P] = [P]_0 - [BOZ] \qquad eq\ (12)$$

where $[P]_0$ is the initial concentration of phenol. In the case of benzoxazine synthesis from formaldehyde, phenols and primary amines, the main reactions of formaldehyde-amine derivatives are the reactions which occur with phenol[13]. Almost all of the consumed phenol is converted into benzoxazine and little side reactions of phenol occurred as mentioned previously. In other words, almost all of formaldehyde-amine derivatives are converted into benzoxazine. The concentration of formaldehyde-amine derivatives at a given time, [*FAD*], can be obtained from

$$[FAD] = [FAD]_0 - [BOZ] \qquad eq\ (13)$$

In this work, $[FAD]_0=[A]_0=1$ mol/kg, and the initial concentration of phenol is also 1 mol/kg, then $[FAD]_0=[A]_0=[P]_0=1$ mol/kg. eq (13) can be expressed as:

$$[FAD] = [FAD]_0 - [BOZ] = [P]_0 - [BOZ] \qquad eq\ (14)$$

Then, eq (11) becomes

$$\frac{d[BOZ]}{dt} = k([P]_0 - [BOZ])^{\alpha+\beta} = k([P]_0 - [BOZ])^{\chi} \qquad eq\ (15)$$

where $\alpha+\beta=\chi$, and χ denotes overall reaction order of benzoxazine synthesis. The integral formula of eq (15) can be written as eq (16).

$$\int_0^t d[BOZ] = \int_0^t k([P]_0 - [BOZ])^{\chi}\, dt \qquad eq\ (16)$$

Where t denotes reaction time. The relationship between benzoxazine concentration and reaction time can be obtained from eq (16)

$$[BOZ] = [P]_0 - \left\{[P]_0 - k(1-\chi)t\right\}^{\frac{1}{1-\chi}} \qquad eq\ (17)$$

In this work, the initial concentration of phenol was 1 mol/kg, therefore, the plots about the concentrations of phenol and benzoxazine versus reaction time were constructed using the data in Fig. 2 in conjunction with eq (17) (see Fig. 3). And the fitted reaction rate constants and reaction orders were listed in Table 1.

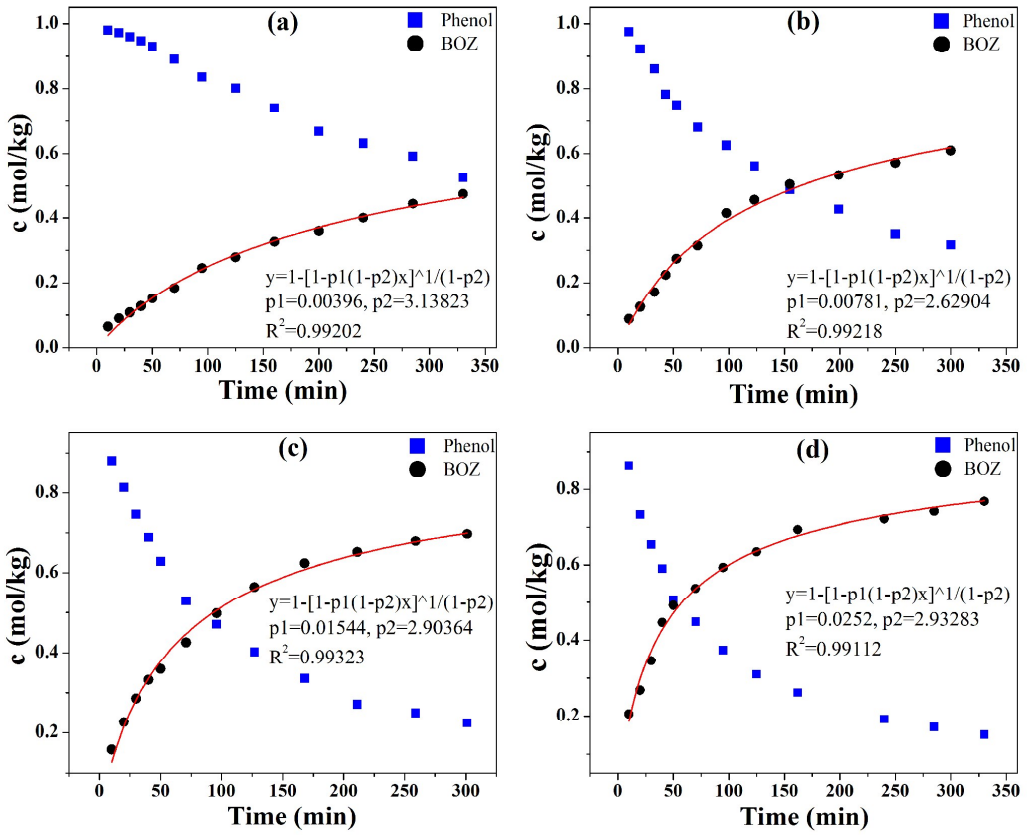


Fig. 3 Concentrations of phenol and benzoxazine versus reaction time at different temperatures. (a) 60 °C, (b) 70 °C, (c) 80 °C, (d) 90 °C.

Table 1 Rate constants k and reaction order χ at various temperatures.

Temperature (°C)	$k\times10^4(s^{-1})$	Reaction order χ
60	0.66	3.14
70	1.30	2.63
80	2.57	2.90
90	4.20	2.93

According to the results, reaction temperatures did not change the synthesis mechanism but varied the reaction rate. Benzoxazine synthesis reaction was assigned to the model of n-order reaction (approximately *3*-order reaction), and the rate

constants, k, increased with the reaction temperature increased.

Assuming that the reaction order, χ, was 3, the plots about the concentrations of benzoxazine versus reaction time were reconstructed using the data in Fig. 2 in conjunction with eq (17) (see Fig. S5). All of the fitting factors, R^2, exceed 0.99, suggesting these fittings were reasonable. And the fitted reaction rate constants were listed in Table 2.

Table 2 Rate constants k at various temperatures (χ=3).

Temperature (°C)	$k\times10^4$(s^{-1})
60	0.64
70	1.46
80	2.68
90	4.34

The rate constants, k, can be expressed in *Arrhenius* form,

$$\ln k = \ln A - \frac{E_a}{RT} \qquad eq\ (18)$$

where E_a is activation energy, J/mol; A is the pre-exponential factor; T is absolute temperature, K^{-1}; R is the universal gas constant, 8.314 $J\cdot mol^{-1}\cdot K^{-1}$. Hence, the *Arrhenius* curve can be plotted using the data in Table 2 in conjunction with eq (18) (see Fig. 4). The activation energy of benzoxazine synthesis, E_a=64.04 kJ/mol, can thus be obtained from the slope of ln$k$~1/T curve.

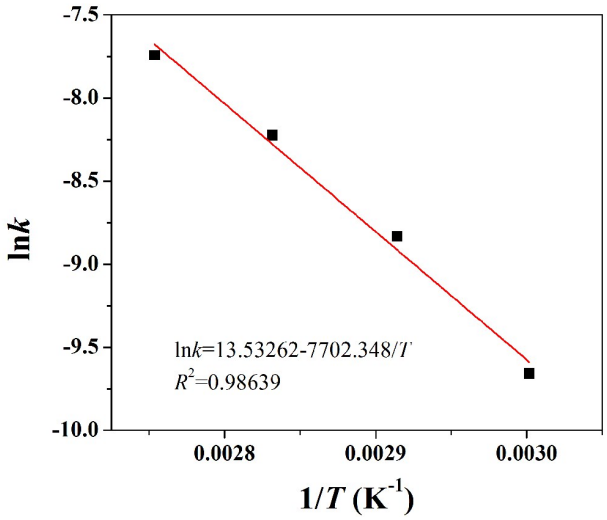


Fig. 4 The *Arrhenius* curve for the benzoxazine synthesis from phenol, *n*-propylamine and formaldehyde.

As mentioned previously, we aim to seek the key starting material through probing the kinetic of benzoxazine formation and phenol consumption. The kinetic parameters of phenol consumption were therefore studied. According to derivation of eq (12) and eq (14), the initial concentration of phenol ($[P]_0$=1 mol/kg), then

[*BOZ*]=[*P*]$_0$-[*P*]=1-[*P*], [*FAD*]=[*FAD*]$_0$-[*BOZ*]=1-[*BOZ*]. Fitting [*BOZ*] and [*FAD*] into eq (11), eq (19) can be obtained

$$\frac{d([P]_0-[P])}{dt}=-\frac{d[P]}{dt}=k[P]^{\alpha'+\beta'}=k'[P]^{\chi'} \quad \text{eq (19)}$$

where *k'* denotes the rate constant of benzoxazine synthesis; $\alpha'+\beta'=\chi'$, and χ' denotes overall reaction order of benzoxazine synthesis. The integral formula of eq (19) can be written as eq (20).

$$\int_0^t d[P]=\int_0^t -k'[P]^{\chi'}dt \quad \text{eq (20)}$$

where *t* denotes reaction time. The relationship between phenol concentration and reaction time can be obtained from eq (20)

$$[P]=[k'(\chi'-1)t+1]^{\frac{1}{1-\chi'}} \quad \text{eq (21)}$$

According to previous fitting, the reaction order $\chi'=\chi=3$. Then the plots about the phenol concentrations versus reaction time were constructed using the data in Fig. 2 in conjunction with eq (21) (see Fig. S6). And the fitted reaction rate constants were listed in Table 3. The reaction rate constants of phenol consumption at 60 ^{o}C, 70 ^{o}C, 80 ^{o}C and 90 ^{o}C were respectively 0.62×10^4 s^{-1}, 1.48×10^4 s^{-1}, 2.80×10^4 s^{-1} and 4.42×10^4 s^{-1}, while the sets of the reaction rate constants of phenol-*n* propylamin-based benzoxazine formation were successively 0.66×10^4 s^{-1}, 1.30×10^4 s^{-1}, 2.57×10^4 s^{-1} and 4.20×10^4 s^{-1}. The reaction rate constants of phenol consumption approximately equaled to those of benzoxaine formation. This probably proved that phenol was the key starting material in the synthesis of phenol-*n* propylamin-based benzoxazine from formaldehyde, phenol and primary amines.

Table 3 Rate constants *k'* at various temperatures (χ'=3).

Temperature (°C)	$k'\times10^4$(s^{-1})
60	0.62
70	1.48
80	2.80
90	4.42

Similarly, the *Arrhenius* curve was plotted by using the data in Table 3 in conjunction with eq (18) (see Fig. 5). The activation energy (E_a' = 66.12 kJ/mol) of phenol consumption can thus be obtained from the slope of ln*k*~1/*T* curve. E_a' is close to E_a of benzoxazine formation. This further proved that phenol was possibly the key starting material and played an important role in benzoxazine synthesis. Since phenol mainly reacted with formaldehyde-amine derivatives to generate mannich bases, the step of the reaction between formaldehyde-amine derivatives and phenol (*step 2*) was possibly the key step.

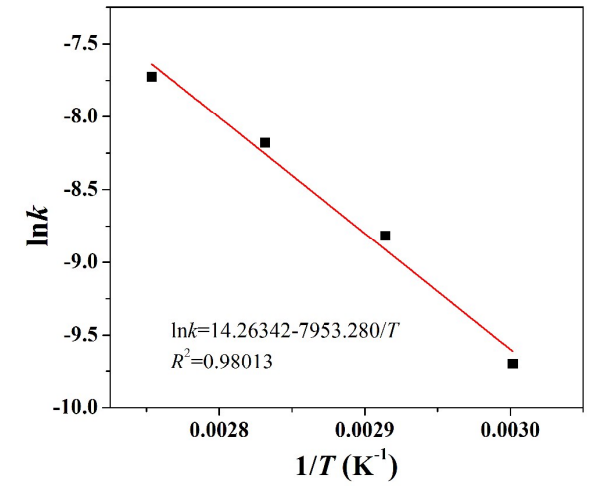


Fig. 5 The *Arrhenius* curve for phenol consumption.

5. Conclusions

In this work, reaction kinetics of benzoxazine synthesis from phenol, *n*-propylamine, and formaldehyde with the aim of identifying the key starting materials and the controlling step were investigated. The formation rates of benzoxazine approximately equal to the consumption rates of phenol. The kinetic parameters of benzoxaznine synthesis, such as reaction order, reaction rate constants, and activation energy, were found to approximately equal to those of phenol consumption. The results suggested that phenol was the key starting material and played an important role in the synthesis of benzoxazine. Furthermore, the step of the reaction between formaldehyde-amine derivatives and phenol for the production of mannich bases (*step 2*) was the controlling step. This finding is anticipated to help researchers understand and control the synthesis of benzoxazines for a better design of novel benzoxazines.

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The kinetic parameters of benzoxaznine synthesis approximately equaled to those of phenol consumption revealed that phenol was the key starting materials.