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Synthesis and kinetics of 2,5-dicyanofuran in the presence of hydroxylamine ionic liquid salts

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ABSTRACT

2,5-Dicyanofuran (DCF) is an important biomass-derived platform compound primarily used to prepare bio-based adiponitrile, which is the key precursor for the synthesis of nylon 66 and 1,6-hexanediisocyanate (HDI). In this study, one-pot, green and safe synthesis of DCF from 2,5-diformylfuran (DFF) and hydroxylamine ionic liquid salts was proposed. Eco-friendly hydroxylamine ionic liquid salts were used as the nitrogen source. Ionic liquid exhibited three-fold function of co-solvent, catalysis and phase separation. The conversion of DFF and yield of DCF reached 100% under the following optimum reaction conditions: temperature of 120 °C for 70 min, volume ratio of paraxylene: $[HSO_3\text{-b-Py}]\cdot HSO_4$ of 2:1, and molar ratio of DFF:$(NH_2OH)_2\cdot[HSO_3\text{-b-Py}]\cdot HSO_4$ of 1:1.5. The reaction mechanism for the synthesis of DCF was proposed, and the kinetic model was established. The reaction order with respect to DFF and intermediate product 2,5-diformylfuran dioxime (DFFD) was 1.06 and 0.16, and the reaction activation energy was 64.07 $kJ\cdot mol^{-1}$ and 59.37 $kJ\cdot mol^{-1}$ respectively. After the reaction, the ionic liquid was easy to separate, recover and recycle.
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1. Introduction

Nitriles are highly versatile compounds, which act as not only precursors in the synthesis of spices, pesticides, and pharmaceuticals, but also intermediates in the preparation of various functional compounds [1,2]. 2,5-Dicyanofuran (also known as 2,5-furandiformonitrile, DCF), is an important bio-based platform compound and is often used as a 'bridge' to link bioresources to high value-added petrochemicals [3,4]. As an intermediate of nitrogenous compound, DCF is highly relied upon in the synthesis of bio-based adiponitrile through hydrogenation and ring-opening reactions [5]. Adiponitrile is a crucial precursor for the synthesis of nylon-66 and high-end polyurethane raw material 1,6-hexanediisocyanate (HDI). Nylon-66 is widely used in the plastic and chemical fiber industries, whereas HDI is utilised in automobile and coating industries [6–8].

DCF is typically prepared through the cyanidation of halide substrates [9–11], which is accompanied by severe challenges, such as harsh reaction conditions, strong toxicity, and large amounts of the waste generated. In recent years, the alternative method for DCF synthesis from 5-hydroxymethylfurfural (5-HMF) and 2,5-diformylfuran (DFF) have attracted the attention of researchers. Xu *et al.* [12] proposed direct conversion from 5-HMF into DCF by using oxidant O_2. The reaction involved three steps: oxidation, amination and dehydration. The operational conditions employed as follows: MnO_2 catalyst, 1.6 MPa O_2, the reaction temperature of 130 °C and reaction time of 5 h; the yield of DCF was 95%. Xu *et al.* [9] synthesized DCF from DFF and $NH_2OH\cdot HCl$. First, 2,5-diformylfuran dioxime (DFFD) was obtained from the oximation of DFF in water in the presence of the NaOAc catalyst, with a yield of 90%. The resulting DFFD was dehydrated at 120 °C for 6 h to obtain DCF in the acetonitrile solvent with amberlyst-15 catalyst, the yield of DCF was 82%.

Ionic liquids (ILs) have been widely researched as green solvents and catalysts [13] for the characteristics of good solubility, designability, high thermal stability and non-volatility. Imran *et al.* has conducted a serious of studies on the application of ionic liquids. For example, the utility of ionic liquids in the chemical science, such as extraction, separation, electro-analysis and spectroscopic studies were studied in detail [14]. The novel bioactive imidazolium ionic liquids halides were developed and showed high antimicrobial activity against the Staphylococcus aureus strain in the inhibition zone tests [15]. Ionic liquid iron nanocomposite particles were prepared and exploited as sorbent for

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removal of propranolol drug residue in water. The maximum removal of propranolol was 90% [16]. Additionally, ionic liquids have also been investigated for high performance liquid chromatography and capillary electrophoresis [17]. Furthermore, ILs were used as alternatives to conventional inorganic acids in hydroxylamine stabilization, leading to the formation of several eco-friendly hydroxylamine ionic liquid salts with high reactivity in various clean synthesis reactions [18–21].

At present, the synthesis of DCF from bio-based platform compounds also suffers from various constraints, such as long reaction times, low product yields, pollution caused by metal salt catalysts and corrosive raw materials, and safety risks related to flammability and explosions. Therefore, the development of an eco-friendly and safe method for DCF preparation is critical. Targeting green, safe and sustainable methods, Wang *et al.* firstly proposed a novel approach (Fig. 1) to prepare bio-based adiponitrile from 5-HMF through the synthesis and transformation of DCF. The specific process is dehydrogenation of 5-HMF into DFF, followed by the one-pot synthesis of DCF from DFF and hydroxylamine ionic liquid salts. Further hydrogenation and ring opening of DCF are processed to synthesize adiponitrile and hexanediamine [5,22–24].

This study mainly focused on the synthesis of DCF with DFF and hydroxylamine ionic liquid salts. The obtained DCF can be further used for the sustainable, clean and safe synthesis of bio-based adiponitrile. In addition, the previously developed eco-friendly hydroxylamine ionic liquid salts [19,20] were used to replace the corrosive hydroxylamine inorganic acid salts as the nitrogen source. The IL was used as the catalyst, co-solvent and phase separation agent to realize the efficient and green synthesis of DCF. After the reaction, the IL was easy to separate, recover, and recycle.

2. Experimental

2.1. Materials and reagents

DFF (>98%) was purchased from Shanghai Aladdin Biochemical Technology Co. Ltd. DCF (95%) was obtained from Shanghai Bide Pharmaceutical Technology Co. Ltd. Paraxylene (AR) and hydroxylamine sulfate (99%) were procured from Shanghai Yien Chemical Technology Co. Ltd. NaOH (AR) was obtained from Tianjin Kermel Chemical Reagent Co. Ltd. Ascorbic acid (>97%) was from Tianjin No.1 Chemical Reagent Factory. Pyridine (AR) was from Tianjin Guangfu Fine Chemical Research Institute. 1,4-butanesulfonolactone (97%) was from Tianjin Xiensi Biochemical Technology Co. Ltd. All materials were used without further purification.

2.2. Catalytic reactions

The hydroxylamine ionic liquid salts were prepared as reported in literature [18,20]. Generally, DFF, hydroxylamine ionic liquid salts, ionic liquid and paraxylene were placed in a three-necked flask equipped with a reflux condenser and a mechanical stirrer, and the mixture was heated to the target temperature and stirred for 100 min. The first sample was withdrawn when the target temperature was reached. The succeeding samples were drawn at 5 min intervals until the last sample at 100 min. The samples were analyzed in an Aligent GC 7890B gas chromatography equipped with a DB-WAX capillary column (30 m × 0.32 mm × 0.25 μm) and a flame ionization detector. The parameters were set as: N_2 carrier, 320 °C FID temperature, 250 °C injection port temperature. The program-controlled column temperature was as follows: hold the initial temperature at 90 °C for 1 min, then increase the temperature at a rate of 15 °C·min^{-1} to 225 °C, then hold for another 1 min. The conversion of DFF, and yield of DCF were evaluated by the area-normalization technique as shown in Eqs. (1)–(3):

$$Y_{DCF} = \frac{A_{DCF} \cdot f_{DCF}}{\sum_1^n A_i \cdot f_i} \times 100\% \quad (1)$$

$$Y_{DFFD} = \frac{A_{DFFD} \cdot f_{DFFD}}{\sum_1^n A_i \cdot f_i} \times 100\% \quad (2)$$

$$X_{DFF} = 1 - \frac{A_{DFF} \cdot f_{DFF}}{\sum_1^n A_i \cdot f_i} \times 100\% \quad (3)$$

where, Y_{DCF} is the yield of DCF, Y_{DFFD} is the yield of DFFD, X_{DFF} is the conversion of DFF, A_i and f_i is the peak area and relative correction factor of corresponding substance, respectively.

2.3. Kinetic equation fitting

According to the experimental results, the differential kinetic equation of the synthesis of DCF from DFF and hydroxylamine ionic liquid salts was fitted and the parameters of the experimental data at different temperatures were estimated using lstOpt analysis software.

2.4. Characterization

The chemical structure of the organic compounds was analyzed by Aligent 7890B-5977A GC–MS. The ^{1}H NMR and ^{13}C NMR spectra of the organic compounds were recorded on a Bruker AVANCE 400 MHz NMR spectrometer using DMSO-d_6 as the solvent and

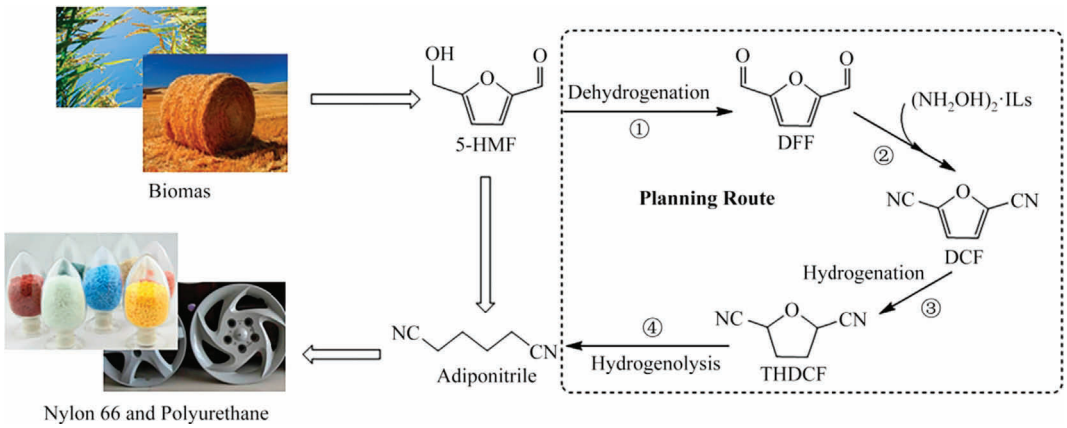

Fig. 1. New process for the synthesis of bio-based adiponitrile from 5-HMF.

TMS as the standard. The FT-IR spectra was recorded using a NICOLET NEXUS 470 Fourier infrared spectrometer from 4000-400 cm^{-1} in either liquid film or KBr tablet form.

3. Results and Discussion

3.1. Direct synthesis of DCF from DFF and hydroxylamine ionic liquid salts

The effects of different hydroxylamine salts on the synthesis of DCF were studied and the results were summarized in Table 1. These hydroxylamine salts include hydroxylamine ionic liquid salts such as hydroxylamine 1-sulfobutyl-3-methyl imidazole hydrosulfate salt ($(NH_2OH)_2$·[HSO_3-b-mim]·HSO_4), hydroxylamine 1-sulfobutyl pyridine hydrosulfate salt ($(NH_2OH)_2$·[HSO_3-b-Py]·HSO_4) and *N*,*N*,*N*-tri-methyl-*N*-sulfobutyl hydrosulfate salt ($(NH_2OH)_2$·[HSO_3-b-$N(CH_3)_3$]·HSO_4), and the typical hydroxylamine inorganic acid salts $(NH_2OH)_2·H_2SO_4$ and $NH_2OH·HCl$. From Table 1, it can be seen that $(NH_2OH)_2$·[HSO_3-b-mim]·HSO_4 and $(NH_2OH)_2$·[HSO_3-b-Py]·HSO_4 exhibited superior reactivity. The DFF conversion and the resulting yield of DCF were both 100%, which were much higher than those using $(NH_2OH)_2·H_2SO_4$. A DCF yield of 34.1% was obtained when $(NH_2OH)_2$·[HSO_3-b-$N(CH_3)_3$]·HSO_4 was used, which was slightly lower than that of $(NH_2OH)_2·H_2SO_4$. When $NH_2OH·HCl$ was used, no DCF was detected. The primary byproducts of the reactions whose DCF yield are not 100% are 5-cyanofuraldehyde oxime and 5-cyano-furaldehyde, which were the results of incomplete dehydration and cyanation. The reaction performance of these hydroxylamine ionic liquid salts were as follows: $(NH_2OH)_2$·[HSO_3-b-$N(CH_3)_3$]·HSO_4<$(NH_2OH)_2$·[HSO_3-b-mim]·HSO_4= $(NH_2OH)_2$·[HSO_3-b-Py]·HSO_4, which was in accordance with the acid strength order of the three ionic liquids, [HSO_3-b-$N(CH_3)_3$]·HSO_4 < [HSO_3-b-mim]·HSO_4≈[HSO_3-b-Py]·HSO_4 [19,25], indicating that the reaction performance of the hydroxylamine ionic liquid salt depended greatly on the acid strength of the corresponding ionic liquid. The higher acid strength facilitated the dehydration process and the higher DCF yield. Hence, compared to the hydroxylamine inorganic acid salts, $(NH_2OH)_2$·[HSO_3-b-mim]·HSO_4 and $(NH_2OH)_2$·[HSO_3-b-Py]·HSO_4 demonstrated much higher reactivities. Moreover, $(NH_2OH)_2$·[HSO_3-b-Py]·HSO_4 was selected as an alternative hydroxylamine salt for the synthesis of DCF due to the significantly higher cost of $(NH_2OH)_2$·[HSO_3-b-mim]·HSO_4.

In order to determine the role of ionic liquid, differing amounts of paraxylene and [HSO_3-b-Py]·HSO_4 on the DCF synthesis were investigated. From Table 2, upon adding only paraxylene, a large amount of white grains were dispersed in the solution, which corresponded to the undissolved $(NH_2OH)_2$·[HSO_3-b-Py]·HSO_4. This dispersion indicated that paraxylene alone could not adequately dissolve the $(NH_2OH)_2$·[HSO_3-b-Py]·HSO_4, which restricted the reaction between DFF and hydroxylamine, and thereby limited the DCF yield to 48.9%. When the ionic liquid, [HSO_3-b-Py]·HSO_4, was added, the mixture gradually became entirely liquid with two visible phases, which could be attributed to the fact that [HSO_3-b-Py]·HSO_4 was in favor of the dissolution of the hydroxylamine salt, and thereby, gradually increasing the yield of DCF. More specifically, when 4 ml of [HSO_3-b-Py]·HSO_4 was added, the yield of DCF reached 100%. These results revealed that [HSO_3-b-Py]·HSO_4 not merely acted as a co-solvent to promote the dissolution of the hydroxylamine salt, but also as a catalyst to improve the yield of DCF. However, optimal amount of ionic liquid could be determined. When an excess of ionic liquid was added, other byproducts were formed and the yield of DCF reduced. After the reaction, the ionic liquid and paraxylene simultaneously separated into two visible phases, which trivializes the recycling process. Therefore, preparing DCF from DFF can be simplified to a one-step, efficient and clean synthesis by incorporating an ionic liquid, which functions three-fold as co-solvent, catalyst and phase separation agent.

The effects of molar ratio between DFF and $(NH_2OH)_2$·[HSO_3-b-Py]·HSO_4 on synthesis of DCF were investigated. Moreover, the utilization rate of N in $(NH_2OH)_2$·[HSO_3-b-Py]·HSO_4 at the different molar ratios was also calculated. As shown in Table 3, the yield of DCF was merely 61.6% when the molar ratio of DFF to $(NH_2OH)_2$·[HSO_3-b-Py]·HSO_4 was 1:1. Increasing the molar ratio, also increased the yield of DCF. When the molar ratio of DFF:$(NH_2OH)_2$·[HSO_3-b-Py]·HSO_4 reached 1:1.5, the yield of DCF reached 100% while the nitrogen-atom utilization was 66.7%, which was almost the maximum. Therefore, 1:1.5 was the optimal mole ratio between DFF and $(NH_2OH)_2$·[HSO_3-b-Py]·HSO_4. This mole ratio is far lower than the feed ratio of ammonia and aldehydes in the synthesis of nitriles *via* the ammoxidation of aldehydes [26], and can effectively avoid the tedious ammonia-recovery process.

3.2. Effects of temperature on the synthesis of DCF

The DCF synthesis reaction were undertaken at 80 °C, 90 °C, 100 °C, 110 °C and 120 °C. The results of reaction temperature on the DFF conversion were presented in Fig. 2. The conversion of DFF was merely 13.9% at 80 °C after 5 min, while DFF was nearly complete conversion at 120 °C after 5 min. These results indicate that the conversion of DFF increased as the temperature raising from 80 °C to 120 °C. By extending the reaction time, the conversion after 100 min can reach 100% at each of the five reaction tem-

Table 1
Effect of different hydroxylamine salts on direct synthesis of DCF①

No.	Hydroxylamine salts	X_{DFF}/%	Y_{DCF}/%
1	$(NH_2OH)_2$·[HSO_3-b-mim]·$HSO_4$②	100	100
2	$(NH_2OH)_2$·[HSO_3-b-Py]·$HSO_4$③	100	100
3	$(NH_2OH)_2$·[HSO_3-b-$N(CH_3)_3$]·$HSO_4$④	100	34.1
4	$(NH_2OH)_2·H_2SO_4$③	100	48.9
5	$NH_2OH·HCl$③	100	0

① Reaction conditions: DFF 3.6 mmol, *n*(DFF):*n*(NH_2OH) = 1:3, paraxylene 8 ml, IL 4 ml, 120 °C, 100 min.
② IL is [HSO_3-b-min]·HSO_4.
③ IL is [HSO_3-b-Py]·HSO_4.
④ IL is [HSO_3-b-$N(CH_3)_3$]·HSO_4.

Table 2
Effect of different amount of paraxylene and ionic liquid on direct synthesis of DCF

No.	Paraxylene/ml	[HSO_3-b-Py]·HSO_4/ml	X_{DFF}/%	Y_{DCF}/%
1	12	0	100	48.9
2	10	2	100	79.0
3	8	4	100	100
4	6	6	100	92.5
5	4	8	100	78.9

Reaction conditions: DFF 3.6 mmol, *n*(DFF):*n*(NH_2OH) = 1:3, 120 °C, 100 min.

Table 3
Effect of mole ratio of DFF to $(NH_2OH)_2$·[HSO_3-b-Py]·HSO_4 on the synthesis of DCF

No.	*n*(DFF):*n*($(NH_2OH)_2$·[HSO_3-b-Py]·HSO_4)	X_{DFF}/%	Y_{DCF}/%	N atom utilization
1	1:1	100	61.6	61.6%
2	1:1.2	100	80.2	66.8%
3	1:1.5	100	100	66.7%
4	1:2	100	100	50.0%

Reaction conditions: DFF 3.6 mmol, paraxylene 8 ml, [HSO_3-b-Py]·HSO_4 4 ml, 120 °C, 100 min

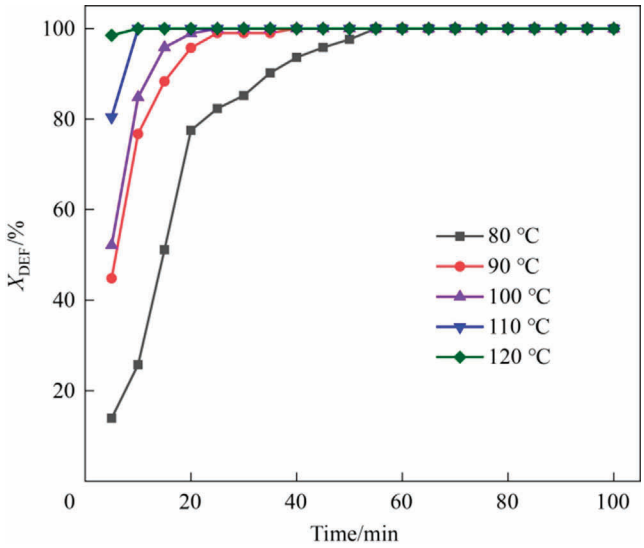

Fig. 2. Effects of reaction temperature on the conversion of DFF. Reaction conditions: DFF 14.4 mmol, $(NH_2OH)_2$·[HSO_3-b-Py]·HSO_4 21.6 mmol, paraxylene 32 ml, [HSO_3-b-Py]·HSO_4 16 ml.

peratures. However, the time to 100% conversion were 70 min and 10 min at 80 °C and 120 °C, respectively. These results suggest that higher reaction temperature quickens the reaction rate, and shortens the time required to reach complete conversion of DFF.

The effects of reaction temperature on the yield of DCF were explored. As shown in Fig. 3, at 80 °C, DCF was detected after 60 min and with a low yield of only 8.2%. As the reaction temperature increased, DCF was detected earlier and the yield was greater. When the reaction temperature was 120 °C, DCF was detected at 5 min, and its yield was maximized at 70 min. Furthermore, increasing the reaction temperature steepens the yield curve of DCF. These results conclusively suggest that higher reaction temperatures are conducive to the synthesis of DCF.

Gas chromatography analysis showed that in addition to the expected solvent paraxylene, raw material DFF and target product DCF, another compound was detected (Fig. S1: t = 14.094 in Supplementary Material). According to the GC–MS result (Fig. S2), the molecular weight of the compound was 154.05, which corresponds to 2,5-diformylfuran dioxime (DFFD). Literature has reported that DFFD can appear as an intermediate product in DCF synthesis from DFF and hydroxylamine, which can be further dehydrated to produce DCF [9,27].

The effect of the reaction temperature on the DFFD yield was also investigated and shown in Fig. 4. The yield of DFFD demonstrated a trend of initially increasing, then decreasing as the reaction temperature increased. The time required for the yield of DFFD to reach the maximum value was shortened significantly as the reaction temperature increased, which was also similar to the time required for the complete conversion of DFF (Fig. 2). Moreover, the DFFD yield gradually decreased, then became undetectable after 70 min at 120 °C. Accordingly, the 100% DCF yield was also reached after 70 min at 120 °C (Fig. 3). Thus, at low temperatures, the reaction between DFF and hydroxylamine primarily yielded DFFD; while higher temperatures favored the dehydration of DFFD to produce DCF.

In summary, the effects of different reaction parameters on the synthesis of DCF were investigated, and the reaction conditions can be optimized as follows: 14.4 mmol DFF, 21.6 mmol $(NH_2OH)_2$·[HSO_3-b-Py]·HSO_4, 32 ml paraxylene, 16 ml [HSO_3-b-Py]·HSO_4, 120 °C reaction temperature and 70 min reaction time. Under these conditions, the conversion of DFF and the yield of DCF were both 100%.

3.3. Plausible reaction mechanism

The mechanism for one-pot synthesis of DCF from DFF and $(NH_2OH)_2$·[HSO_3-b-Py]·HSO_4 was surmised through the experimental and characterization results. Based on literatures [9,28,29], aldoxime could be easily generated from the reaction between aldehyde and hydroxylamine salt, and the aldoxime can be further dehydrated to form nitrile [30,31]. Within this process, the intermediate, DFFD, was detected, which suggested a two-step reaction: DFF reacted with $(NH_2OH)_2$·[HSO_3-b-Py]·HSO_4 to form the intermediate DFFD, which was then dehydrated to DCF in the presence of the ionic liquid. A step-by-step experiment was designed to verify the hypothesis, and the plausible reaction mechanism was proposed.

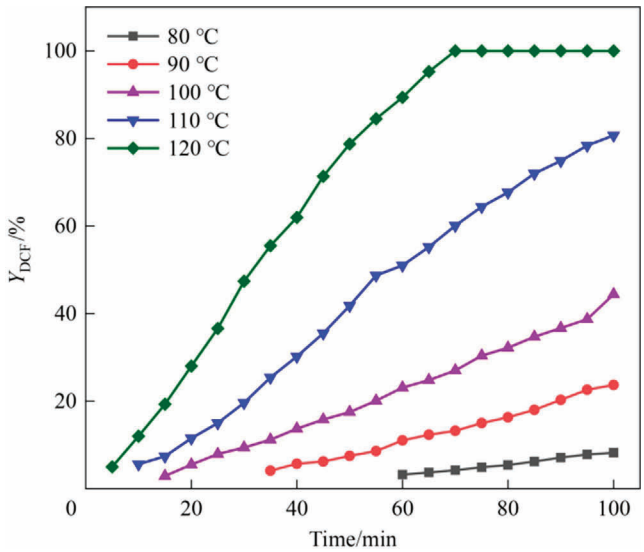

Fig. 3. Effects of reaction temperature on the yield of DCF. Reaction conditions: DFF 14.4 mmol, $(NH_2OH)_2$·[HSO_3-b-Py]·HSO_4 21.6 mmol, paraxylene 32 ml, [HSO_3-b-Py]·HSO_4 16 ml.

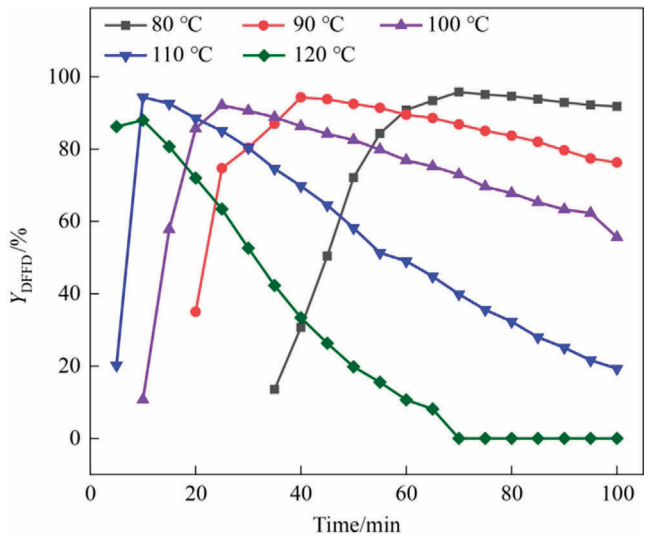

Fig. 4. Effect of reaction temperature on the yield of DFFD. Reaction conditions: DFF 14.4 mmol, $(NH_2OH)_2$·[HSO_3-b-Py]·HSO_4 21.6 mmol, paraxylene 32 ml, [HSO_3-b-Py]·HSO_4 16 ml.

(1) Synthesis of DFFD from DFF and $(NH_2OH)_2$·[HSO_3-b-Py]·HSO_4. DFF (3.6 mmol), $(NH_2OH)_2$·[HSO_3-b-Py]·HSO_4 (5.4 mmol) and water (8 ml) was charged into the flask fitted with a reflux condenser and a mechanical stirrer. Subsequently, the mixture was heated to 55 °C in a water bath and stirred for 30 min. After the reaction, the mixture was left to cool to room temperature. The white powder was precipitated, filtered and dried to obtain DFFD (MS: m/z = 154 (Fig. S2); FT-IR: 3020 cm^{-1} (=C-—H), 3188 cm^{-1}, 2860 cm^{-1}(O-—H), 1630 cm^{-1}(C=N), 935–1026 cm^{-1}(-CN-—O) (Fig. S4); ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.09 (s, 1H), 7.58 (s, 1H), 7.31 (s, 1H) (Fig. S5); ^{13}C NMR (101 MHz, DMSO-d_6) δ 144.42 (s,1C), 135.11 (s,1C), 118.31 (s,1C) (Fig. S6)), which was consistent with the structure reported in the literature [32].

(2) Synthesis of DCF from DFFD catalyzed by ionic liquid. DFFD (3.6 mmol), ionic liquid [HSO_3-b-Py]·HSO_4 (4 ml) and paraxylene (8 ml) were initially mixed in a flask. The mixture was heated in an oil bath at 120 °C for 70 min. After the reaction, the organic phase of the solution was evaporated to remove the solvent. Afterwards, n-hexane was added and heated to 50 °C for 10 min. After cooled to room temperature and filtered, DCF was obtained as a white solid by filtration (MS: m/z = 118 (Fig. S3); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.87 (s, 1H) (Fig. S7); ^{13}C NMR (101 MHz, DMSO-d_6) δ 128.82 (s,1C), 124.12 (s,1C), 110.11 (s,1C) (Fig. S8)).

From these experiments, it could be seen that DFF reacts with $(NH_2OH)_2$·[HSO_3-b-Py]·HSO_4 to initially form DFFD, then, DFFD is further dehydrated to form DCF under the catalysis of ionic liquid. The plausible mechanism is depicted in Fig. 5.

Firstly, as the reaction temperature increases, NH_2OH and [HSO_3-b-Py]·HSO_4 are discharged due to the decomposition of $(NH_2OH)_2$·[HSO_3-b-Py]·HSO_4, where the NH_2OH reacts with aldehyde groups from DFF to form DFFD. Finally, the generated DFFD is thoroughly contacted by external mixing with the ionic liquid and dehydrated to form DCF. The ionic liquid here includes not only the added ionic liquid later, but also the ionic liquid released from the decomposition of $(NH_2OH)_2$·[HSO_3-b-Py]·HSO_4.

3.4. Reaction kinetic model

3.4.1. Establishing of the kinetic model

The intermediate product DFFD was detected, indicating that the preparation of DCF involved multiple elementary reactions. Based on the reaction mechanism proposed above, a two-step kinetic model for the synthesis of DCF in a batch reactor was conceived. To simplify the reaction model, the following assumptions could be made [33]:

(1) Only DFF, DFFD and DCF exists in the reaction system; any side reactions were not considered.

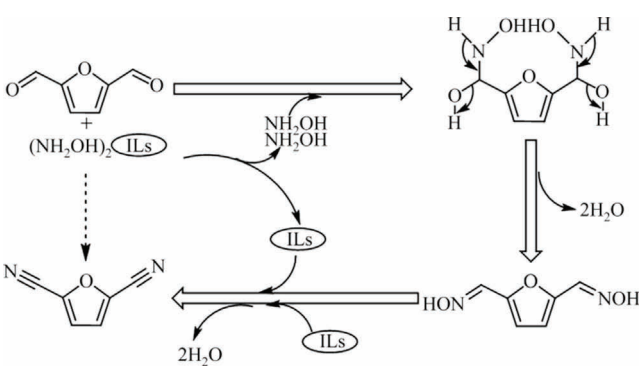

Fig. 5. Plausible reaction mechanism.

(2) The stirring was kept constant at 250 r·min^{-1}, which would eliminate the influence of phase interface. The influence of diffusion may be ignored.

(3) The sampling amount was negligible compared to the total volume, and the process can be considered to be under constant volume conditions.

During the reaction, the concentration of DFF decreased while the concentration of DFFD had a maximum, and the amount of DCF increased. This trend was in accord with the characteristics of series reaction [34,35]. Thus, the reaction process can be described with the following equation:

$$\underset{\text{A}}{\text{DFF}} + \underset{\text{B}}{(NH_2OH)_2\cdot\text{ILs}} \xrightarrow{k_1} \underset{\text{I}}{\text{DFFD}} \xrightarrow{k_2} \underset{\text{P}}{\text{DCF}}$$

Since the initial amount of $(NH_2OH)_2$·[HSO_3-b-Py]·HSO_4 was in excess of DFF, its concentration could be regarded as a constant and the influence of $(NH_2OH)_2$·[HSO_3-b-Py]·HSO_4 on the reaction rate was included in the modified rate constant. The rate equation of the two-step reaction can be expressed as:

$$r_A = -\frac{dc_A}{dt} = k_1 c_A^{\alpha} \tag{4}$$

$$r_P = \frac{dc_P}{dt} = k_2 c_I^{\gamma} \tag{5}$$

$$\gamma_I = \frac{dc_I}{dt} = k_1 c_A^{\alpha} - k_2 c_I^{\gamma} \tag{6}$$

where, k_1 and k_2 are the rate constants of the oximation reaction of DFF in the first step and the dehydration reaction of DFFD in the second step, respectively. r_A is the consumption rate of DFF, r_P is the formation rate of DCF, and r_I is the reaction rate of the intermediate DFFD; c is the instantaneous concentration of the corresponding substance; α and γ are the reaction order of the first and second step, respectively.

3.4.2. Estimation of parameters

Utilizing the on-line sampling results, the differential kinetic equation was solved by lstOpt analysis software to obtain the estimated parameters (See Supplementary Material for calculation program, operation results and results of kinetic experiments, Table S1–S5). The experimental data at 90 °C, 100 °C, 110 °C and 120 °C were fitted, and the parameters of the kinetic equation were estimated by using the least-square integration method to obtain the kinetic data (Table 4).

In this reaction, the effect of temperature on the reaction rate is in accord with the Arrhenius equation

$$k = k_0 \exp\frac{-E_a}{RT} \quad \text{or} \quad \ln k = -\frac{E_a}{RT} + \ln(k_0) \tag{7}$$

where E_a is the reaction activation energy, and k_0 is the pre-exponential factor.

Table 4
Estimation of kinetic parameters

Temperature/K	α	γ	k_1	k_2
363.15	0.9725	0.2999	0.1308	0.0016
373.15	1.0746	0.3104	0.1999	0.0028
383.15	1.0631	0.0031	0.3796	0.0037
393.15	1.1115	0.0430	0.6403	0.0075

The relationships between ln(k)-1/T (Fig. 6) and related data (Table 5) were extracted by plotting ln(k) *vs.* 1/t and using linear fitting.

Through the above calculations, the kinetic equations (Eqs. (8) and (9)) of one-pot synthesis of DCF from DFF and $(NH_2OH)_2$-·[HSO_3-b-Py]·HSO_4 were obtained. The rationality of the kinetic equations was verified (Fig. S9, Table S6).

$$r_A = 2.04 \times 10^8 \exp\left(-6.41 \times 10^4/RT\right) c_{DFF}^{1.06} \quad (8)$$

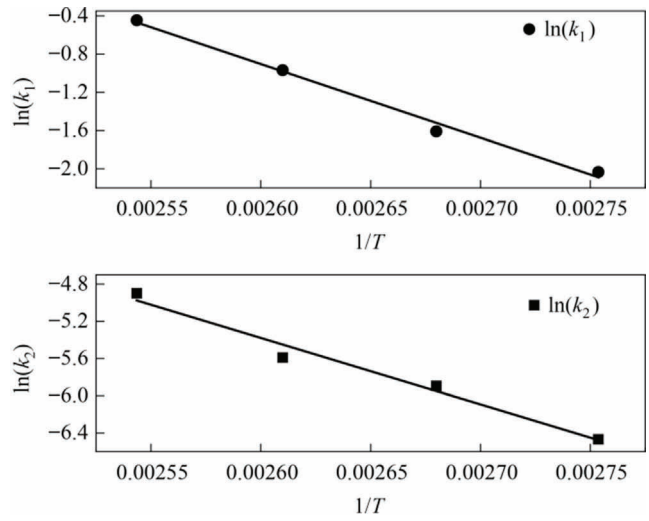

Fig. 6. Relationship between ln(k) and1/T.

Table 5
Calculated values of E_a and k_0

k	Relationship	R^2	E_a/kJ·mol^{-1}	k_0
k_1	$y_1 = -7706.95x + 19.134$	0.9921	64.07	2.04×10^8
k_2	$y_2 = -7141.31x + 13.189$	0.9777	59.37	5.35×10^5

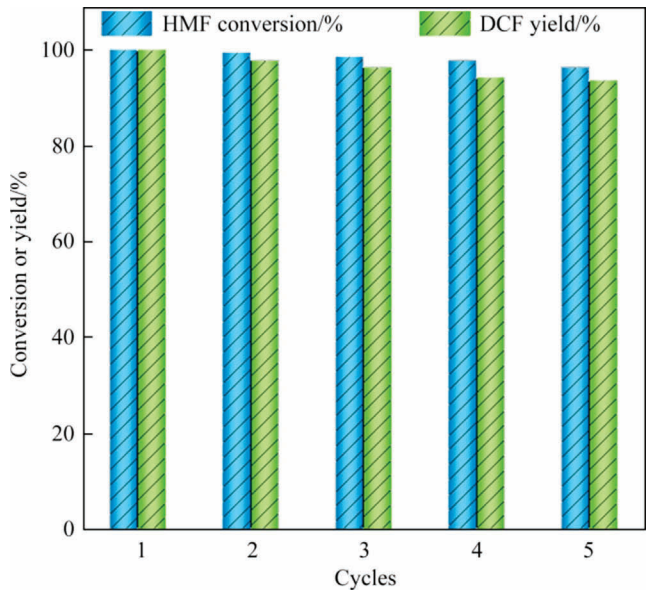

Fig. 7. Recycling of ionic liquid for the synthesis of DCF. Reaction conditions: DFF 3.6 mmol, n(DFF):n(NH_2OH) = 1:3, paraxylene 8 ml, [HSO_3-b-Py]·HSO_4 4 ml, 120 °C, 70 min.

$$r_P = 5.35 \times 10^5 \exp\left(-5.94 \times 10^4/RT\right) c_{DFFD}^{0.16} \quad (9)$$

3.5. Recovering and recycling of the ionic liquid

To investigate the prospect of recovery and recycling of the ionic liquid, the synthesis of DCF was conducted under the optimized reaction conditions (Fig. 7). The resulting mixture was cooled at ambient conditions, while spontaneously segregated into aqueous phase and organic phase. The organic phase was analyzed *via* gas chromatography, while the ionic liquid was recycled as co-solvent and catalyst for the next usage directly without any other treatment. When the ionic liquid was recycled for five times, the conversion of DFF remained as high as 96.4% and the yield of DCF stayed at 93.7%, confirming the incredible stability of [HSO_3-b-Py]·HSO_4.

4. Conclusions

Clean and safe synthesis of DCF from DFF and hydroxylamine ionic liquid salts was achieved with 100% DFF conversion and DCF yield. ILs was used as catalyst, co-solvent and phase separation agent. This novel route presents milder reaction conditions, higher product yield, safer operation and more eco-friendly, which are the advantageous to the previous systems. A plausible reaction mechanism, i.e. DFF oximation to produce DFFD, which then dehydrated to form DCF was proposed. Moreover, the kinetic model was established as follows: $r_A = 2.04 \times 10^8 \exp(-6.41 \times 10^4/RT) c_{DFF}^{1.06}$ and $r_P = 5.35 \times 10^5 \exp(-5.94 \times 10^4/RT) c_{DFFD}^{0.16}$. This study solved a crucial step in the production of bio-adiponitrile, and provided a foundation for its industrial application.

Data Availability

No data was used for the research described in the article.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary Material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cjche.2021.12.026.

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