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Kinetics and quantum chemical study for cyclotrimerization of propanal catalyzed by Brönsted acidic ionic liquids

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ABSTRACT

Several Brönsted acidic ionic liquids (BAILs) were synthesized and used as catalysts for the cyclotrimerization of propanal. The acidity of different BAILs was explored and a preliminarily study of the relationship between catalytic activity and acidity was performed. The kinetics for the BAILs-catalyzed cyclotrimerization of propanal was studied systemically to determine the kinetic model and the kinetic parameters by taking [BSTMG][HSO_4] as the representative catalyst. The effects of various parameters such as catalyst loading, reaction temperature on the kinetics were examined in detail. Besides, the structures of three representative BAILs and the interactions between propanal molecule and ionic pairs of BAILs were studied by means of quantum chemistry calculations.

1. Introduction

Cyclotrimerization of aldehydes is one of the most important reactions in chemical, biological and pharmaceutical industries, and the products (1,3,5-trioxanes) have been implicated in a host of practical applications: as flavoring agents [1]; as stabilizers in color photography [2]; as insecticides [3]; as carriers for scents, deodorants and repellents [4] and as synthetic precursors to complex dendritic molecules, such as the dendrimer [5]. Conventionally, the cyclotrimerization of aldehydes is generally catalyzed by Brönsted or Lewis acids such as H_3PO_4 [6], $TaCl_5$ [7] and other catalysts such as Keggin-type heteropolyacids [8]. However, many of these catalysts suffer from one or more limitations such as corrosion of equipment, tedious isolation of catalyst-product and tendency to deactivation. Hence, the development of highly efficient, easily separable, ‘greener’ catalysts for the reaction is still highly desired.

Ionic liquids (ILs), owing to their unique characteristics, such as low vapor pressure, excellent chemical and thermal stability, recoverability and convenience in product separation, have been applied and found to be effective in some catalytic conversions [9–13]. Brönsted acidic ionic liquids (BAILs) are an interesting subset of ILs which have been reported as novel eco-benign catalysts for some acid catalyzed reactions [14]. Recently, BAILs have been exploited successfully as catalysts for cyclotrimerization reactions and have received effective results [15–17]. However, to the best of our knowledge, the basic research about kinetics for the cyclotrimerization of aldehydes catalyzed by BAILs is still absent.

Therefore, several BAILs were synthesized and their catalytic behavior was investigated by using the cyclotrimerization of propanal as a model system (Scheme 1), additionally, the reaction kinetics was also studied in this article. Based on the results from experimental and theoretical investigation kinetic model was built and the rate constant, activation energy and pre-exponential factor were obtained. Besides, in order to better understand the behavior of BAILs at molecular level, the interactions between propanal molecule and ionic pairs of the representative BAILs were discussed according to their minimum-energy geometries determined by quantum chemical calculations.

2. Experimental

2.1. Synthesis and characterization of BAILs

The BAILs used in this article (Fig. 1) were synthesized according to previously reported synthesis procedures [14,18,19]. The synthetic procedure to prepare [BSTMG][HSO_4] is given here as an example:

[BSTMG][HSO_4]: 1,1,3,3-tetramethylguanidine (0.2 mol) and 1,4-butane sultone (0.2 mol) were charged into a 250 mL round bottom flask equipped with a reflux condenser. Then the mixtures were stirred at 353 K for 7 h. The obtained white solid zwitterion was washed several times with toluene to remove non-ionic residues

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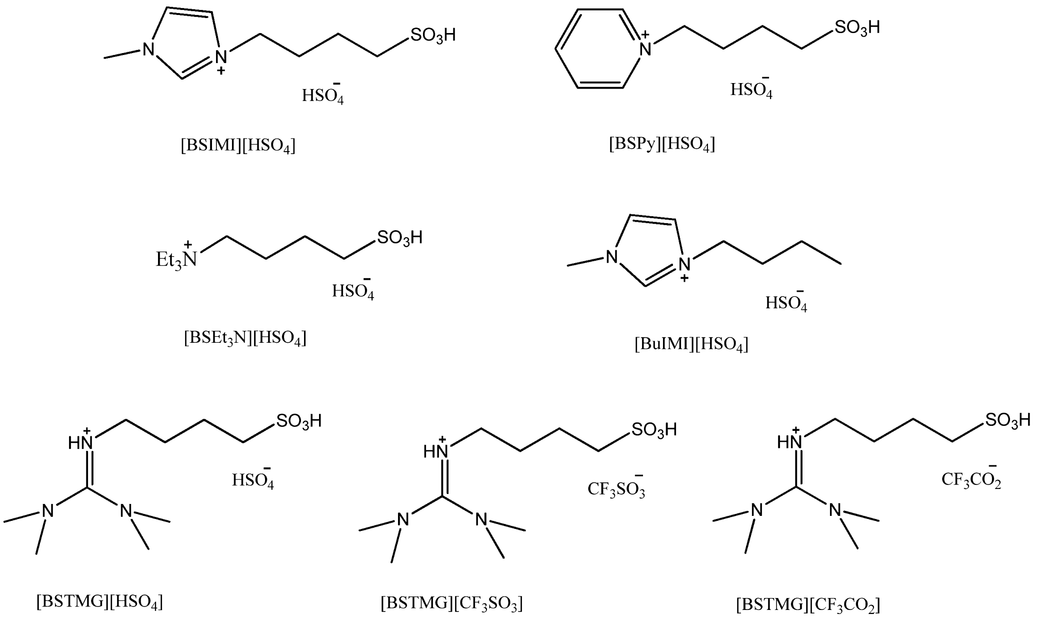


Fig. 1. Structures of Brönsted acidic ionic liquids.

and dried in vacuum. After that, a stoichiometric amount of sulphuric acid (0.2 mol) was added dropwise and the mixture was stirred for 10 h at 343 K. A kind of viscous ionic liquid phase was obtained and was washed by ether for several times. The ionic liquid was dried in vacuum for 2 h. The ionic liquids [BSTMG][CF_3SO_3], [BSTMG][CF_3CO_2], [BSPy][HSO_4], [BSIMI][HSO_4] and [$BSEt_3N$][HSO_4] were prepared by the same procedure.

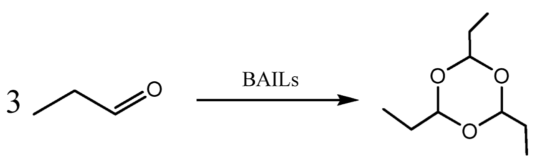
[BSTMG][HSO_4]: IR (KBr, ν/cm^{-1}): 3304, 2948, 1619, 1589, 1461, 1406, 1168, 1039, 887. ^{1}H NMR (400 MHz, D_2O) δ = 2.775–2.750 (s, —CH_3), 1.63–1.51 (m, —CH_2), 3.05 (t, —CH_2—SO_3H), 2.73 (t, —CH_2—N); ^{13}C NMR (400 MHz, D_2O) δ = 21.7 (s, —CH_2—), 28.33 (s, —CH_2—), 39.36 (s, —CH_3), 44.33 (s, —CH_2—N), 50.65 (s, —CH_2—SO_3H), 161.86 (s, C).

[BSPy][HSO_4]: IR (KBr, ν/cm^{-1}): 3136, 3070, 2942, 2948, 1619, 1589, 1461, 1406, 1168, 1039, 887. ^{1}H NMR (400 MHz, D_2O) δ = 2.21–2.26 (m, 2H), 2.79 (t, 2H), 4.56 (t, 2H), 7.84 (t, 2H), 8.30 (t, 1H), 8.62 (d, 2H); ^{13}C NMR (100 MHz, D_2O) δ = 27.2, 48.3, 61.5, 129.7, 145.3, 147.6.

[$BSEt_3N$][HSO_4]: IR (KBr, ν/cm^{-1}): 3450, 2990, 2360, 1710, 1487, 1460, 1397, 1183, 1035. ^{1}H NMR (400 MHz, D_2O) δ = 1.14 (t, 9H), 1.80 (m, 2H), 2.89 (t, 2H), 3.09–3.26 (m, 8H); ^{13}C NMR (100 MHz, D_2O) δ = 9.1, 21.4, 49.1, 53.7, 57.1.

[BSTMG][CF_3SO_3]: IR (KBr, ν/cm^{-1}): 3330, 2950, 1619, 1588, 1459, 1405, 1295, 1228, 1168. ^{1}H NMR (400 MHz, D_2O) δ = 1.41–1.47 (m, 4H), 2.58–2.62 (t, 2H), 2.64 (s, 12H), 2.91 (t, 2H); ^{13}C NMR (100 MHz, D_2O) δ = 21.3, 27.9, 38.9, 43.9, 50.3, 119.6, 161.4.

[BSTMG][CF_3CO_2]: IR (KBr, ν/cm^{-1}): 3276, 2949, 2699, 1771, 1618, 1590, 1457, 1405, 1211, 1158. ^{1}H NMR (400 MHz, D_2O) δ = 1.38–1.50 (m, 4H), 2.63 (t, 2H) 2.66 (s, 12H), 2.94 (t, 2H); ^{13}C NMR (100 MHz, D_2O) δ = 21.6, 28.7,40.5, 45.1, 51.3, 120.8, 163.2, 165.4.



Scheme 1. Cyclotrimerization of propanal catalyzed by BAILs.

For the synthesis of [BuIMI][HSO_4] [20], firstly, [BuIMI]Cl was obtained by the reaction of N-methylimidazole (0.2 mol) with 1-chlorobutane (0.2 mol) in anhydrous dichloromethane at 323–333 K for 5–7 h, then an excess amount of $KHSO_4$ was added to the system and stirred at 343 K for 5–7 h. The solid phase was removed by filtrating and the solvent was evaporated on a rotary evaporator. The transparent ionic liquid was dried under vacuum at 338 K for 6 h.

[BuMIM][HSO_4]: IR (KBr, ν/cm^{-1}): 3418, 3145, 3107, 2961, 1575, 1464, 1380, 1171, 1044, 845. ^{1}H NMR (400 MHz, D_2O) δ = 0.69 (t, 3H), 0.98 (m, 2H), 1.61 (m, 2H), 3.65 (s, 3H), 3.96 (t, 2H), 7.19 (s, 1H), 7.24 (s, 1H), 8.47 (s, 1H); ^{13}C NMR (100 MHz, D_2O) δ = 12.8, 18.9, 31.4, 35.8, 49.5, 122.4, 123.7, 136.0.

2.2. Qualitative and quantitative acidity evaluation of the BAILs

With the help of FT-IR analyses using pyridine as probe molecule the type of acidity of BAILs are investigated. The mixture with a 1:5 mol ratio of pyridine to the studied BAILs was spreaded into the liquid film between KBr windows. All the IR spectra were recorded on a NICOLET 6700 spectrometer. To determine the quantitative acidity of the BAILs, the ionic liquids and the indicator 4-nitroaniline (5 mg/L) were dissolved in distilled H_2O at concentrations of 25 mmol/L and characterized by UV–Vis spectra with a PerkinElmer lambda 650s UV–Vis spectrophotometer.

2.3. Cyclotrimerization reaction

Catalyst was added into a constant temperature reactor equipped with a low-temperature pump (DLSB), propanal was then put into the reactor when temperature reached to the required value. The reaction mixture was stirred at the target temperature, and meanwhile a small amount of samples were taken out from the reactor at regular intervals and analyzed with an Agilent 7890 GC equipped with a FID detector.

2.4. Computational methods

All calculations in our study were performed using the Gaussian 09 program [21]. All the geometries were optimized at the B3LYP/6-31G (d,p) level.

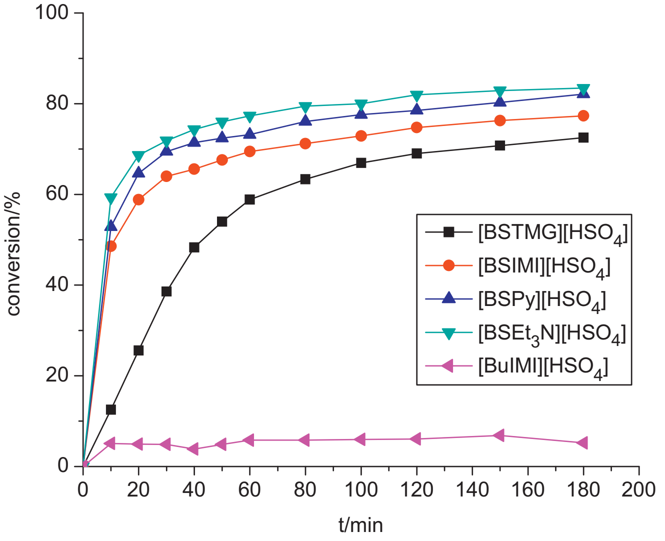


Fig. 2. Cyclotrimerization of propanal to compare the efficiency of different BAILs.

3. Results and discussion

3.1. Effects of different ionic liquids catalysts

In keeping with the tenets of green chemistry, we found that solvent was completely unnecessary for cyclotrimerization. Initial experimentation was undertaken catalyzed by 0.21% (mol ratio based on reactant) of BAILs at 303 K to compare their efficiency and the results are presented in Figs. 2 and 3. It can be seen from Fig. 2 that the initial reaction rate is very high as 70–80% propanal conversion was obtained in the 1 h for [BSIMI][HSO_4], [BSPy][HSO_4] and [$BSEt_3N$][HSO_4]. However the cyclotrimerization reaction was sluggish when [BSTMG][HSO_4] was used as catalyst and the conversion only reached 58% within 1 h. The use of [BuIMI][HSO_4] resulted in very low conversion (about 6%). It is evident from the results that the activity of the BAILs is governed by the functionality (—SO_3H) of BAILs. BAILs having —SO_3H functionalization in cation were found to be more active than the BAILs without —SO_3H functionalization. Compared with other —SO_3H functionalized BAILs catalysts, [BSTMG][HSO_4] exhibits lower initial rate which may be due to the steric hindrance of its guanidinium moiety making it difficult for propanal to get close to the catalyst. Fig. 3 shows the effect of anion structure on the conversion of propanal. Results show that [BSTMG][CF_3SO_3] was found to be the best compared with [BSTMG][HSO_4] and [BSTMG][CF_3CO_2].

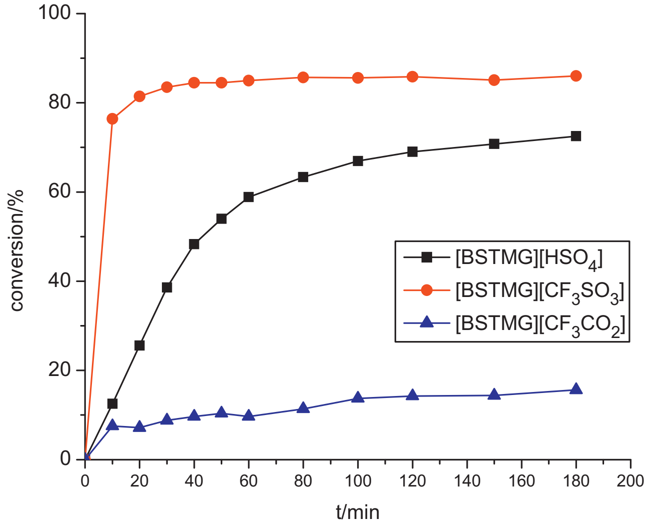


Fig. 3. Evolution of propanal conversion with time in the cyclotrimerization catalyzed by [BSTMG][CF_3SO_3], [BSTMG][HSO_4] and [BSTMG][CF_3CO_2].

Table 1
Calculation and comparison of H_0 values of different BAILs in distilled H_2O.

Entry no.	ILs	A_{max}	[I] (%)	[IH$^+$] (%)	H_0
1	[BSIMI][HSO_4]	0.349	76.4	23.6	1.500
2	[BSPy][HSO_4]	0.347	75.9	24.1	1.488
3	[$BSEt_3N$][HSO_4]	0.345	75.5	24.5	1.479
4	[BuIMI][HSO_4]	0.416	91.0	9.0	1.995
5	[BSTMG][HSO_4]	0.346	75.7	24.3	1.483
6	[BSTMG][CF_3SO_3]	0.372	81.4	18.6	1.631
7	[BSTMG][CF_3CO_2]	0.489	92.3	7.7	2.065
8	Blank	0.457	100	0	–

Indicator: 4-nitroanline (5 mg/L, pK_a = 0.99) and BAILs (25 mmol/L).

These experiment results demonstrated that the acidity and structure of ionic liquids were important contributors to catalytic activities. In order to explore the relationship between catalytic activity and acidity, the acidity of BAILs was evaluated.

3.2. The relationship of catalytic activity and acidity

A few efforts have been made to characterize and determine the Brönsted acidity of ionic liquids. It is reported that using pyridine as a probe molecule the acidity type of ionic liquid could be characterized [22]. Pyridine can react with the Brönsted acid and produce a pyridinium ion. The pyridinium ion has an absorption peak near 1540 cm^{-1} in the FT-IR spectra. As shown in Fig. 4, the IR spectrum of pyridine mixed ionic liquid exhibits an additional band near 1540 cm^{-1} indicating the presence of Brönsted acid sites.

The acidic scales of BAILs studied here were conducted on a PerkinElmer lambda 650s UV–Vis spectrophotometer with a basic indicator 4-nitroaniline according to the procedure reported in the literature [23–25]. Based on a protocol that was first proposed by Gilbert et al. in 2003 on the basis of the Hammett acidity function. The Hammett acidity function, H_0, was calculated by using the equation: $H_0 = pK(I)_{aq} + \log([I]/[IH^+])$. This value was regarded as the relative acidity of the IL [26]. Where "I" represents the indicator, [I] and [IH$^+$] are respectively the molar concentrations of the unprotonated and protonated forms of the indicator, $pK(I)_{aq}$ is the pK_a value of the indicator. Based on the Beer–Lambert law the absorption is proportional to the concentration of absorbing species in the material, and on condition of the same light path length, the ratio of [I]/[IH$^+$] can be calculated by the absorbance difference of basic indicator measured after addition of BAILs. Under the same concentration of 4-nitroaniline (5 mg/L, pK_a = 0.99) and BAILs (25 mmol/L) in distilled H_2O, we determined the H_0 values of the seven BAILs and the results are listed in Table 1.

The results indicated that the acidities of BAILs depended on the characteristics of both cations and anions. Among the BAILs having [HSO_4] anion, the IL [BuIMI][HSO_4] without a —SO_3H group on cation had lower relative acidity of H_0 = 1.995, which results in the poor catalytic activity in cyclotrimerization of propanal in comparison to other BAILs with the same anion. So one can see from this phenomenon that the —SO_3H group played an important role in defining the acidity of the BAILs. The acidities of —SO_3H functionalized BAILs (having same anion of [HSO_4]$^-$) are near each other (Table 1, entries 1–3 and 5), but the differences in their catalytic performance are obvious. Hence, we believe that the acidity of BAILs is not the only factor in determining the catalytic activity. When the cations of the ILs were the same, the dependence of the acidity of the IL on anion was significant. In the case of [BSTMG][HSO_4], [BSTMG][CF_3SO_3] and [BSTMG][CF_3CO_2], the acidity follows

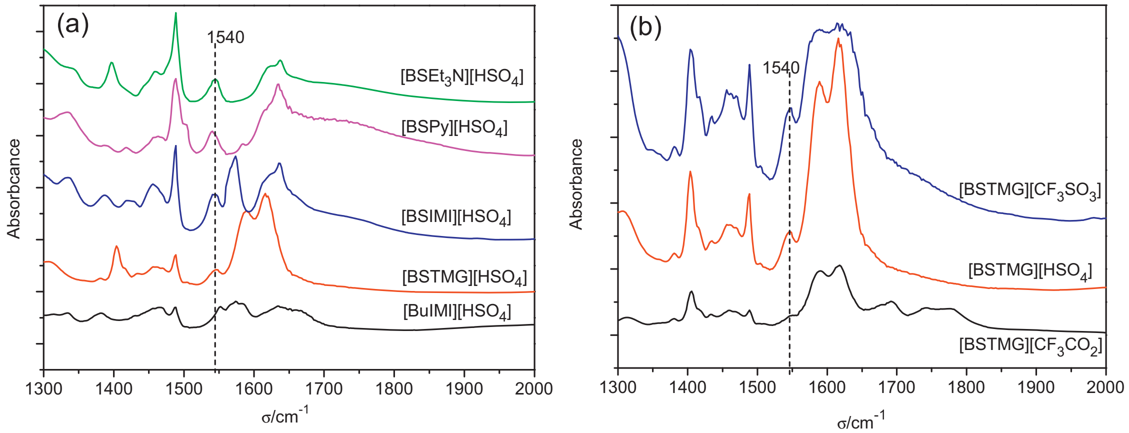


Fig. 4. FT-IR spectra of ionic liquids with pyridine as probe molecule. (a) Ionic liquids with the same anion of $[HSO_4]^-$ and (b) ionic liquids with the same cation of $[BSTMG]^+$.

the order $[BSTMG][HSO_4] > [BSTMG][CF_3SO_3] > [BSTMG][CF_3CO_2]$ which does not completely reflect the order of the catalytic activities of these ionic liquids since the structure of SO_3H-functionalized ionic liquids also influences the reaction activities. Lowest activity was observed for $[BSTMG][CF_3CO_2]$ probably because of weaker acidity. $[BSTMG][CF_3SO_3]$ showed the highest activity in despite of the relatively high H_0 value. At present, the reason for these interesting results remains to be elucidated. Perhaps the weakest nucleophilicity and high stability of $[CF_3SO_3]^-$ favor the coordination of catalyst with propanal and make proton transformation more easy to form the active centers, which then lead to the high activity mentioned above.

3.3. Effects of catalyst loading of BAILs on cyclotrimerization

Cyclotrimerization of propanal in the presence of $[BSTMG][HSO_4]$ ionic liquid was conducted to test the effects of catalyst loading at 298 K. It is obvious that increasing the amount of catalyst is positive to the improvement of conversion of propanal (Fig. 5). The conversion of propanal increases rapidly from 56% to 69% within 210 min with the catalyst loading ranging from 0.01% to 0.05%. However, only a fair change is observed in the conversions of propanal when the dosage is raised from 0.0.5% to 0.38%. And a slight decrease of conversion can be observed when the dosage reached 0.38%. It suggests that the further increase in the amount of catalyst is not very necessary for the conversion of reactants. This may be reasoned that the increase of catalyst loading provides more acidic active sites that are helpful for the generation of active intermediates and the conversion of propanal. However, the conversion of propanal is not improved too much when there exists an excess of catalyst active sites than required by the reactant molecules. Beyond a certain catalyst loading, the conversion of propanal is mainly influenced by chemical reaction equilibrium. Therefore, 0.21% catalyst loading is considered suitable and is used in most of the rest experiments.

3.4. Effects of temperature on cyclotrimerization

The effect of reaction temperature ranging from 273 to 303 K on the conversion of propanal was investigated using $[BSTMG][HSO_4]$ as catalyst. As can be seen from Fig. 6, increasing the reaction temperature was favorable for raising the conversion of propanal. However, because of the limitation of chemical reaction equilibrium, similar conversions of propanal at 3 h are obtained when the temperature is raised from 293 to 303 K, the conversion of propanal cannot continue to be enhanced.

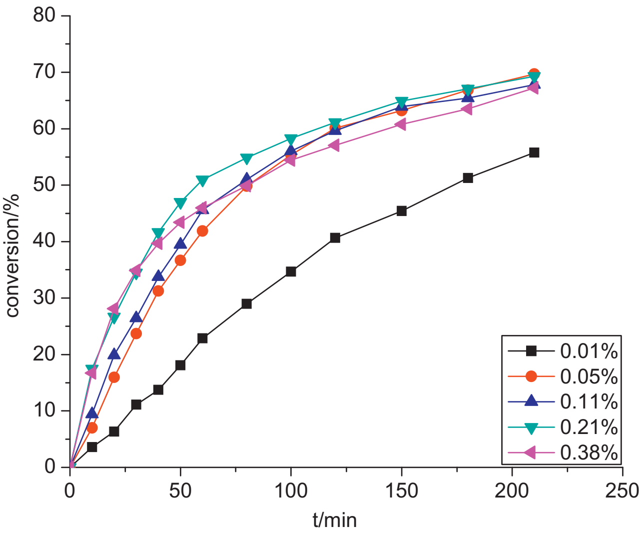


Fig. 5. Effect of catalyst loading on conversion of propanal ranging from 0.01% to 0.38% (mol ratio based on propanal).

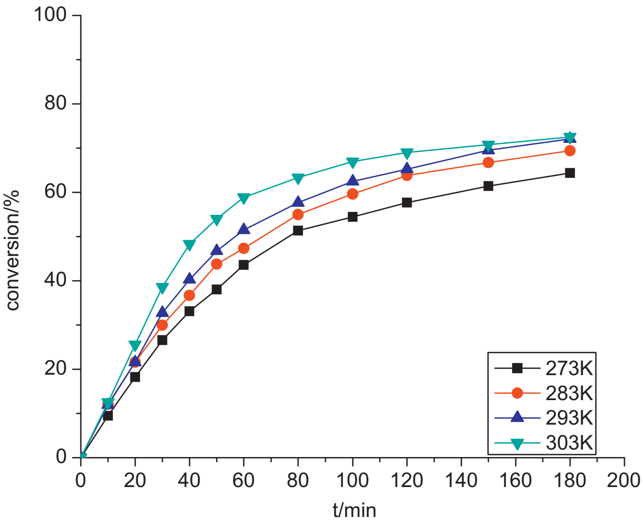


Fig. 6. Effects of reaction temperature on the conversion of propanal over $[BSTMG][HSO_4]$ (0.21%).

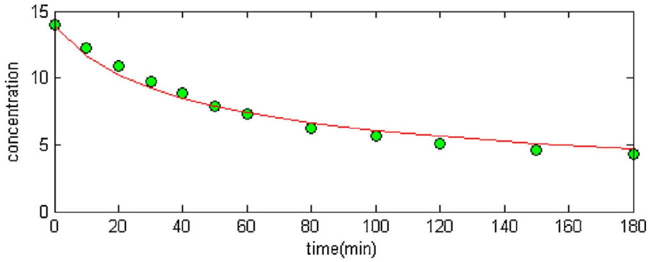


Fig. 7. Comparison of calculated and experimental results for the cyclotrimerization of propanal over [BSTMG][HSO_4] catalyst at 283 K.

3.5. Kinetic studies

Ionic liquids have been found to promote the cyclotrimerization of aldehydes, but the quantitative kinetic model for the synthesis of trioxanes catalyzed by ionic liquids has not been reported systemically. We were therefore encouraged to build kinetic model and obtain kinetic parameters for cyclotrimerization of propanal upon the BAIL catalyst of [BSTMG][HSO_4] based on the former experimental data.

The reaction equation for the cyclotrimerization of propanal can be written as follows:

$$\begin{array}{lll} & 3\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} & \mathrm{B} \\ t=0 & C_{\mathrm{A},0} & 0 \\ t=t & C_{\mathrm{A}} & C_{\mathrm{B}} \end{array}$$

where k_1 and k_{-1} are the rate constants for the forward and reverse reactions, respectively. A and B represent propanal and the product of cyclotrimerization respectively. $C_{A,0}$ is the initial concentration of propanal at the beginning of the reaction, whereas C_A and C_B are the concentrations of A and B in a given reaction time, respectively. The reaction rate equation can be expressed as:

$$r = \frac{-1}{3}\frac{dC_A}{dt} = \frac{dC_B}{dt} = k_1C_A^3 - k_{-1}C_B \quad (1)$$

$$\frac{dC_A}{dt} = -3(k_1C_A^3 - k_{-1}C_B) \quad (2)$$

$$K_e = \frac{k_1}{k_{-1}} \quad (3)$$

where K_e is the equilibrium constant.

Equilibrium constant K_e equals to 3.0795 at the 283 K, which was obtained by experiment. Eq. (2) was numerically integrated by a fourth-order Runge–Kutta algorithm with Matlab. As shown in Fig. 7, the green dots and red curve denote experimental and calculated values, respectively, it shows that the calculated values are in good agreement with the experimental results. Then the reaction rate constants k_1 and k_{-1} based on the model for [BSTMG][HSO_4] catalyst are 3.7013×10^{-5} and 1.2019×10^{-5}, respectively. Thus, the reaction rate equation of cyclotrimerization of propanal can be expressed as:

$$r = k_1C_A^3 - k_{-1}C_B = 3.7013 \times 10^{-5}C_A^3 - 1.2019 \times 10^{-5}C_B$$

For the reason of $C_A^3 \gg C_B$ in the initial stage of the reaction, especially when the reaction temperature was relatively low, the reaction rate equation can be written approximately as:

$$r \approx \frac{-1}{3}\frac{dC_A}{dt} = \frac{dC_B}{dt} = 3.7013 \times 10^{-5}C_A^3 \quad (4)$$

$$\frac{dC_A}{dt} = -3 \times 3.7013 \times 10^{-5}C_A^3 \quad (5)$$

Table 2
C_A C_A” and their ARD values of different time at 283 K.

t (min)	C_A (mol L^{-1})	C''_A (mol L^{-1})	$(C''_A - C_A)/C_A$
0	13.946	13.946	0
10	12.2613	11.6544	−0.0495
20	10.9337	10.2152	−0.0657
30	9.7678	9.2042	−0.0577
40	8.8292	8.4441	−0.0436
50	7.8446	7.8457	0.0001
60	7.3481	7.3588	0.0015
80	6.2813	6.6070	0.0518

The integrated form of Eq. (5) can be written as:

$$\frac{1}{C_A^2} - \frac{1}{C_{A,0}^2} = 2.2208 \times 10^{-4}t \quad (6)$$

If put t into Eq. (6), then we could get C''_A values by calculation, which represent the calculated concentration values of different time at 283 K. For comparison, the values of C_A, C''_A and their averaged relative deviation (ARD) are listed in Table 2.

From Table 2, it is interesting to find that the calculated values C''_A which based on Eq. (6) are in good agreement with the experimental data of C_A with an ARD less than 6% in most of cases at the reaction time under 80 min. The value of ARD is thought to accord within the acceptable limit. Therefore, in the initial period of this reaction, Eq. (4) can be a relatively accurate and convenient substitute for reaction rate equation.

In addition, from the experimental data of propanal conversion under different catalyst loading we calculated the kinetic constant for the reaction. The dependence of the kinetic constant on catalyst concentration is described by a curve with a break (Fig. 8).

We suggest that catalyst forms complexes with propanal and the formation of active centers (M*) in the system under review takes place through an rapid equilibrium reaction of the type of

$$\mathrm{BAIL}\cdots\mathrm{M} \rightleftharpoons \underset{\mathrm{M*}}{\mathrm{C_2H_5\overset{+}{C}HOHA^-}}$$

$$\mathrm{M} = \text{propanal}$$

(A^- is the gegen ion). In terms of this mechanism the break appearing on the curve of the reaction rate constant versus catalyst loading is due to the increased number of active centers stabilized by gegen ions owing to high concentration of the catalyst. The reaction rate constant is positively related to the catalyst loading in a range from 0.05% (mol/mol) to 0.21% (mol/mol) which indicated that more active centers available is beneficial to the reaction rate.

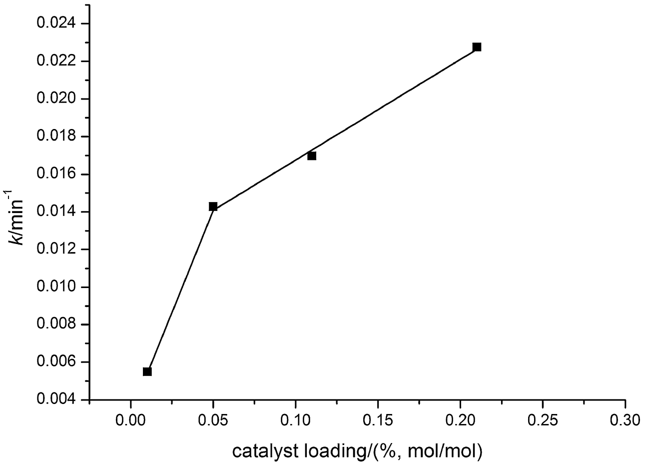


Fig. 8. Relationship of reaction rate constant and catalyst loading.

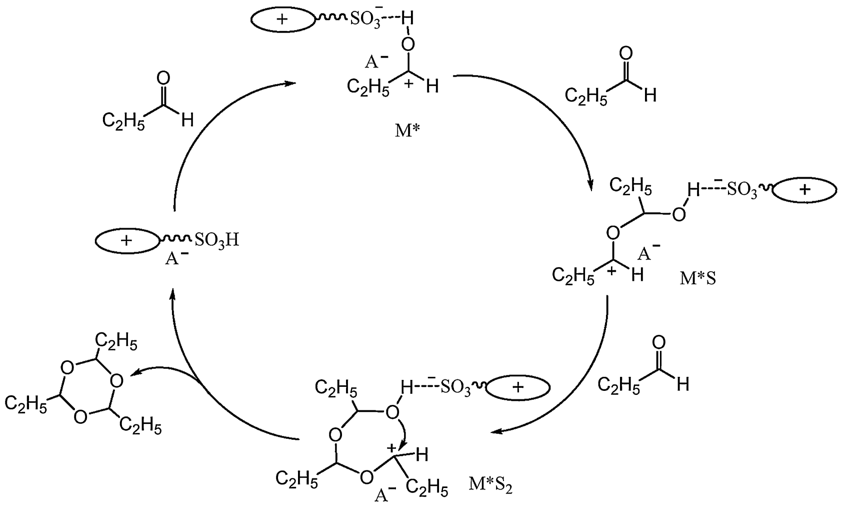


Fig. 9. The proposed catalytic mechanism of cyclotrimerization of propanal.

Based on the kinetic studies of cyclotrimerization of propanal, a proposed mechanism for the trimerization is shown in Fig. 9: first, the BAIL coordinated with propanal, and then proton transferred between propanal and BAIL, the "association carbonium ion" (M*) formed, which was considered as the active species. Then the second propanal molecule reacted with M* to yield the ion M*S. M*S could be attacked by the third propanal molecule to yield the ion M^*S_2, intramolecular nucleophilic reaction of this ion generated the six-membered ring product.

The equilibrium constant, K_e, and the reaction rate constants, k_1 and k_{-1}, in equilibrium (2) and (3) at different temperatures were determined by applying a fourth-order Runge–Kutta algorithm with Matlab to the experimental data. Results are given in Table 3.

The Arrhenius equation describes the relationship between k, T, E_a and A, the frequency factor:

$$k_i = A_i \ \exp\left(\frac{-E_{a,i}}{RT}\right) \tag{7}$$

From the data in Table 3, an Arrhenius plot (Fig. 10) of $\ln k$ vs $(1000/T)$ is constructed by mapping the four data points onto Eq. (7). The values of the activation energy, E_a, and the frequency factor, A, which are determined by using the slope and the intercept of the Arrhenius plot are $E_{a,1}$, 13.5302 kJ/mol; A_1, 0.0115; $E_{a,-1}$, 50.9415 kJ/mol; A_{-1}, 3.1039×10^4.

3.6. Quantum chemical study

In order to better understand the microcosmic structure and properties of BAILs, the interactions between reactant molecule and ion pairs of BAILs, and the relationship between interaction strength and catalytic activity of BAILs, three representative BAILs, $[BSTMG][CF_3CO_2]$, $[BSTMG][HSO_4]$ and $[BSEt_3N][HSO_4]$, had been chosen to explore these properties with a method of density functional theory at B3LYP/6-31G (d,p) level using Gaussian 09 program.

Table 3
Values of K_e, k_1 and k_{-1} at different temperatures.

T (K)	K_e	k_1	k_{-1}
273	4.6473	2.9033×10^{-5}	6.2473×10^{-6}
283	3.0795	3.7013×10^{-5}	1.2019×10^{-5}
293	2.1396	4.2322×10^{-5}	1.9780×10^{-5}
303	0.8728	5.5147×10^{-5}	6.3184×10^{-5}

Fig. 11 shows the optimized geometries for $[BSTMG]^+$, $[BSEt_3N]^+$, $[CF_3CO_2]^-$, $[HSO_4]^-$ and propanal, which calculated at the B3LYP/6-31G (d,p) level of theory. For anions, the atomic net charges of oxygen atoms in them are also shown. The negative charges spread around the oxygen atoms, and the positive charges of the anions are located on the sulfur atom ($[HSO_4]^-$) and carbon atom ($[CF_3CO_2]^-$). The negative charge of oxygen in $[CF_3CO_2]^-$ is very close to each other, but great difference exists in $[HSO_4]^-$. Because the —OH is an electron donating group and the $—CF_3$ is an electron withdrawing group, the total negative charge on the oxygen of $[CF_3CO_2]^-$ is −1.226 e, which is less than that of $[HSO_4]^-$ (−2.441 e). Thus with same cation the interaction of $[HSO_4]^-$ is stranger than that of $[CF_3CO_2]^-$.

A series of ion pair geometries of these three BAILs had been designed by considering the location of related cation and anion. All these designed configurations had been optimized and the fully optimized configurations are given in Fig. 12. Theoretical study confirmed that hydrogen bonding exists in the BAILs. It is obvious that anions interact with the $—SO_3H$ and —NH through O—H···O or N—H···O type hydrogen bonding. Geometrical parameters and hydrogen bonding data of the three BAILs correlate well with their

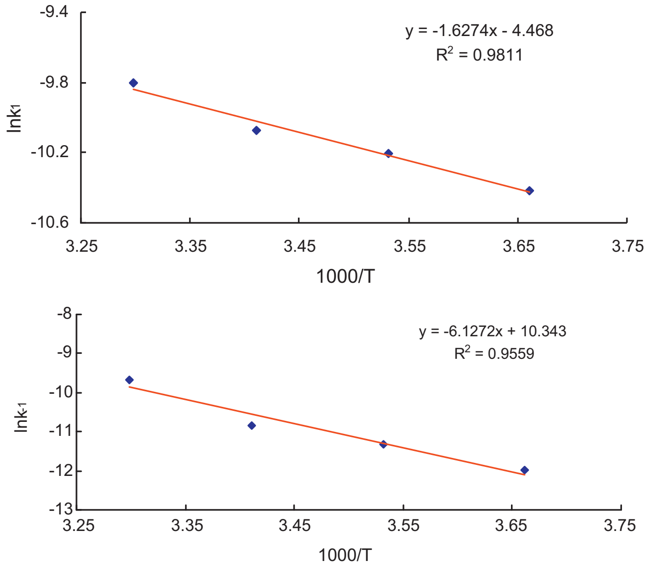
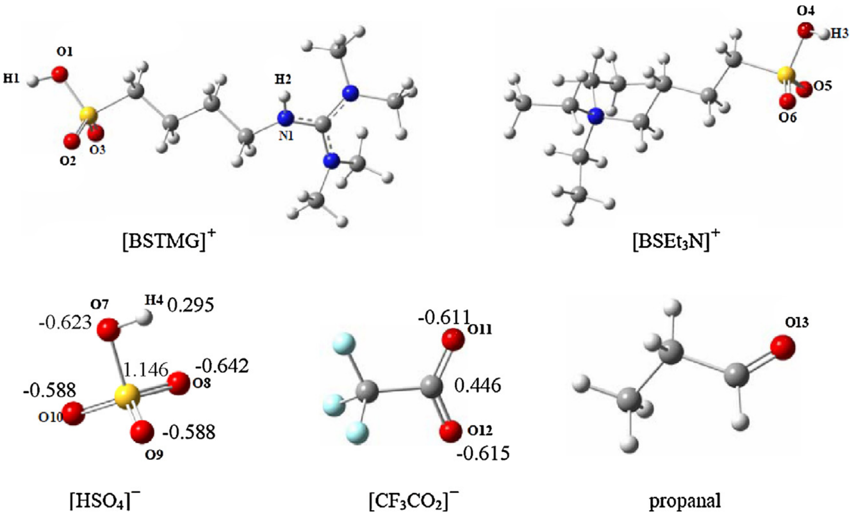


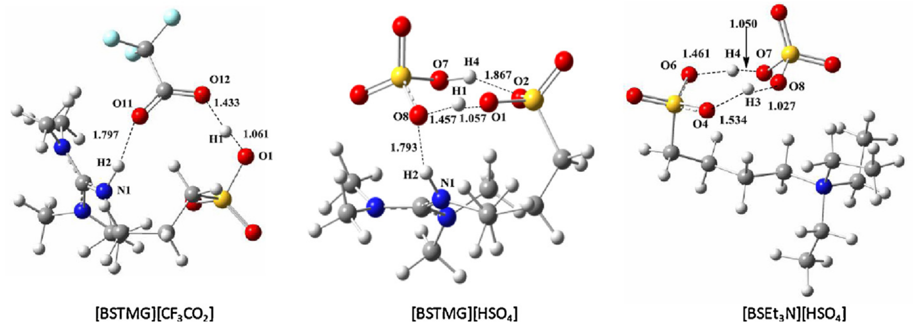
Fig. 10. Arrhenius plot of the reaction over $[BSTMG][HSO_4]$ catalyst.



$[BSTMG]^+$ $[BSEt_3N]^+$

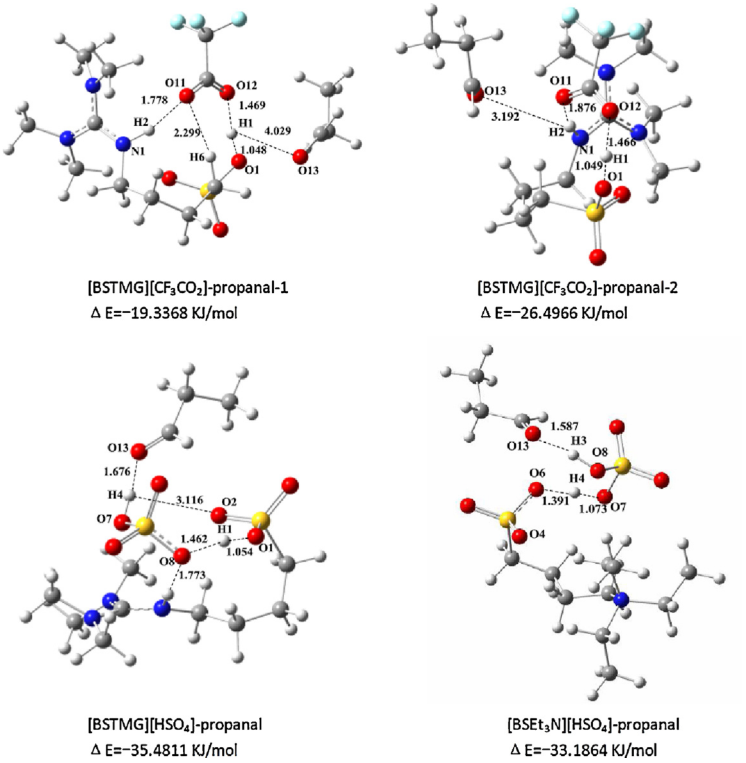
$[HSO_4]^-$ $[CF_3CO_2]^-$ propanal

Fig. 11. Optimized geometries for $[BSTMG]^+$, $[BSEt_3N]^+$, $[CF_3CO_2]^-$, $[HSO_4]^-$ and propanal.



$[BSTMG][CF_3CO_2]$ $[BSTMG][HSO_4]$ $[BSEt_3N][HSO_4]$

Fig. 12. The most stable geometries of $[BSTMG][CF_3CO_2]$, $[BSTMG][HSO_4]$ and $[BSEt_3N][HSO_4]$ ion pairs. Optimized at the B3LYP/6-31G (d,p) level of theory. Bond lengths are in Å.



$[BSTMG][CF_3CO_2]$-propanal-1
Δ E=−19.3368 KJ/mol

$[BSTMG][CF_3CO_2]$-propanal-2
Δ E=−26.4966 KJ/mol

$[BSTMG][HSO_4]$-propanal
Δ E=−35.4811 KJ/mol

$[BSEt_3N][HSO_4]$-propanal
Δ E=−33.1864 KJ/mol

Fig. 13. The representative optimized geometries for the BAILs-propanal complexes. Bond lengths are in Angstrom (Å), ΔE denotes the interaction energy, which $\Delta E = E_{(\text{complexes})} - E_{(\text{BAIL})} - E_{(\text{propanal})}$.

catalytic activity in cyclotrimerization of propanal (Figs. 2 and 3). The higher activity of [BSEt$_3$N][HSO$_4$] is mainly due to the longer bond distance of $H_3 \cdots O_4$ which makes H_3 more labile. Whereas the low activity of [BSTMG][CF$_3$CO$_2$] can be explained based on the significant interaction between H_1 of —SO$_3$H and O_{12} of [CF$_3$CO$_2$]$^-$ ($H_1 \cdots O_{12}$ = 1.433) which inhibits the accessibility of H_1 to the reactant molecules for cyclotrimerization.

The catalytic activity of BAILs was theoretically studied by computing the interaction between the three representative BAILs and propanal. The structures of the complexes of [BSTMG][CF$_3$CO$_2$], [BSTMG][HSO$_4$] and [BSEt$_3$N][HSO$_4$] with propanal molecule are presented in Fig. 13. From Fig. 13, it could be found that the interactions between [BSTMG][CF$_3$CO$_2$] and propanal are very weak with the longer distance between acidic H_1 and O_{13}. So it is hard for propanal to be activated by [BSTMG][CF$_3$CO$_2$], which correlate well with the experimental result that the conversion of propanal is very low by using [BSTMG][CF$_3$CO$_2$] as catalyst (Fig. 3).

As for [BSTMG][HSO$_4$] and [BSEt$_3$N][HSO$_4$], it can be seen in Fig. 13 that the carbonyl group of propanal strongly interacts with the acid proton of the ionic liquid. The distances of $H_4 \cdots O_{13}$ (1.676 Å) in [BSTMG][HSO$_4$]-propanal, and $H_3 \cdots O_{13}$ (1.587 Å) in [BSEt$_3$N][HSO$_4$]-propanal are shorter than the sum of Bondi's van der Waals radii of hydrogen and oxygen (2.72 Å), which reveals that [BSTMG][HSO$_4$] and [BSEt$_3$N][HSO$_4$] can transfer H to propanal to form the active carbonium ion. Compared with [BSTMG][HSO$_4$], the shorter bond length between H_3 and O_{13} (1.587 Å) in [BSEt$_3$N][HSO$_4$]-propanal complexe indicates [BSEt$_3$N][HSO$_4$] is more effective than [BSTMG][HSO$_4$] in cyclotrimerization of propanal which agrees with the experiment results.

4. Conclusion

Several Brönsted acidic ionic liquids have been synthesized and used to catalyze cyclotrimerization of propanal. It was observed that the catalytic activity correlates highly with the acidity and structure of these BAILs. Furthermore, Brönsted acidity of the ionic liquids was evaluated using IR and UV–Vis spectroscopic methods and the kinetic process of cyclotrimerization was investigated over [BSTMG][HSO$_4$] catalyst. With the help of density functional theory (DFT) calculations, the relationship among the structures, acidities and catalytic cyclotrimerization properties of three representative BAILs has also been developed. Hence, these findings give us inspiration to not only take into account the cation framework, but also pay attention to the effect of the anionic partner in the design of functionalized ionic liquid catalyst.

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