Journal of Molecular Catalysis A: Chemical 379 (2013) 86–93

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

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

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ARTICLE INFO

*Article history:*
Received 18 January 2013
Received in revised form 19 July 2013
Accepted 30 July 2013
Available online 8 August 2013

*Keywords:*
Brönsted acidic ionic liquids
Cyclotrimerization
Kinetics study
Quantum chemistry calculations

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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http://dx.doi.org/10.1016/j.molcata.2013.07.021

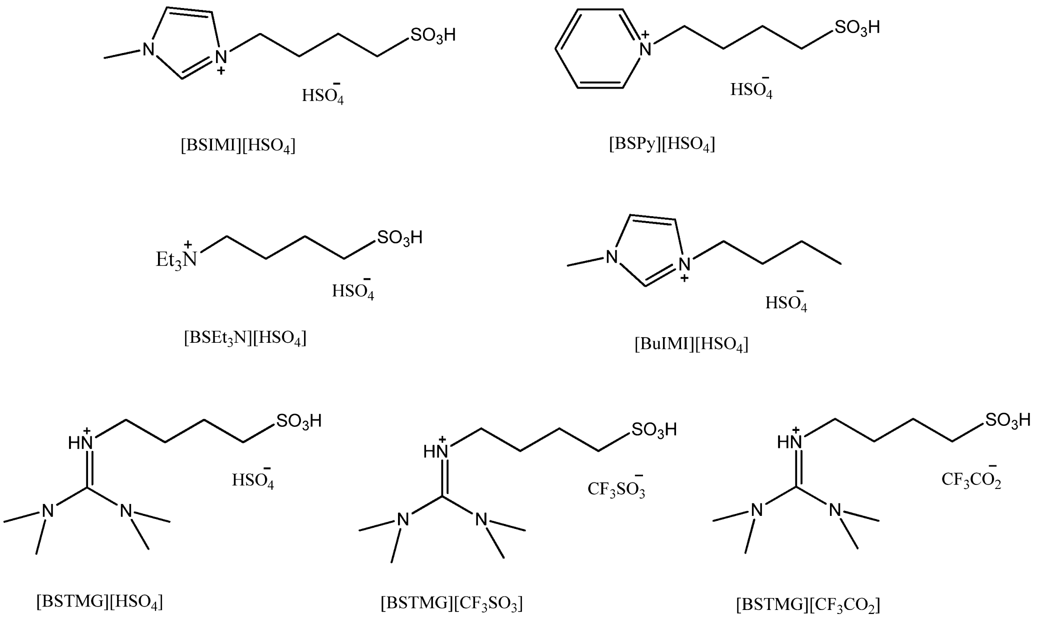


**Fig. 1.** Structures of Brönsted acidic ionic liquids.

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.

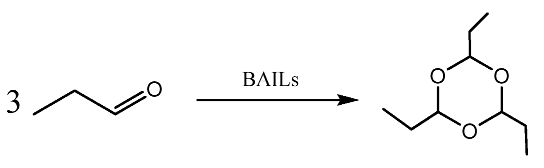
*[BSTMG][$HSO_4$]*: IR (KBr, $\nu$/cm$^{-1}$): 3304, 2948, 1619, 1589, 1461, 1406, 1168, 1039, 887. $^1$H NMR (400 MHz, $D_2O$) $\delta = 2.775–2.750$ (s, $—CH_3$), 1.63–1.51 (m, $—CH_2$), 3.05 (t, $—CH_2—SO_3H$), 2.73 (t, $—CH_2—N$); $^{13}$C NMR (400 MHz, $D_2O$) $\delta = 21.7$ (s, $—CH_2—$), 28.33 (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, $\nu$/cm$^{-1}$): 3136, 3070, 2942, 2948, 1619, 1589, 1461, 1406, 1168, 1039, 887. $^1$H NMR (400 MHz, $D_2O$) $\delta = 2.21–2.26$ (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, $D_2O$) $\delta = 27.2$, 48.3, 61.5, 129.7, 145.3, 147.6.

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

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

*[BSTMG][$CF_3CO_2$]*: IR (KBr, $\nu$/cm$^{-1}$): 3276, 2949, 2699, 1771, 1618, 1590, 1457, 1405, 1211, 1158. $^1$H NMR (400 MHz, $D_2O$) $\delta = 1.38–1.50$ (m, 4H), 2.63 (t, 2H) 2.66 (s, 12H), 2.94 (t, 2H); $^{13}$C NMR (100 MHz, $D_2O$) $\delta = 21.6$, 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, $\nu$/cm$^{-1}$): 3418, 3145, 3107, 2961, 1575, 1464, 1380, 1171, 1044, 845. $^1$H NMR (400 MHz, $D_2O$) $\delta = 0.69$ (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, $D_2O$) $\delta = 12.8$, 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.