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CYCLODEHYDRATION OF DIOLS IN ACIDIC IONIC LIQUIDS

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In the presence of sulfonic acid group functionalized Bronsted-acidic ionic liquids, cyclodehydration of 1,2-ethanediol and 1,4-butanediol is investigated. The role of structure and catalytic activity of ionic liquids on the formation of cyclic ethers: 1,4-dioxane and tetrahydrofuran – is determined.

Key words: *acidic ionic liquids, ethylene glycol, 1,4-butanediol, cyclodehydration, 1,4-dioxane, tetrahydrofuran.*

INTRODUCTION

During the last decades, ionic liquids are extensively used in organic synthesis as solvents and catalysts [1, 2]. Bronsted-acidic ionic liquids (AILs) are used as substitutes of mineral and organic acids in acid-catalyzed reactions like esterification, etherification, pinacol–pinacolone rearrangement, condensation etc. [3–6]. Bronsted-acidic ionic liquids have good proton donor properties comparable with mineral acids. AILs as catalysts are non-corrosive, non-volatile, immiscible with many organic solvents, and they can be recycled and reused [7]. To determine their productivity in diol cyclodehydration, two diols: 1,2-ethanediol (ethylene glycol) and 1,4-butanediol are used. Cyclodehydration of both diols leads to formation of industrially significant cyclic ethers: 1,4-dioxane and tetrahydrofuran (THF). 1,4-Dioxane and THF are widely used as organic solvents. Tetrahydrofuran is a useful solvent for organic synthesis, production of natural and synthetic resins, and also is a valuable intermediate in manufacture of a number of chemicals and plastics. Several traditional preparation methods of these cyclic ethers are based on acid-catalyzed cyclization of corresponding diols [8–12]. The reaction yields depend on reaction conditions. 1,4-Butanediol is very readily cyclized to THF with the elimination of water [10], but in dehydration of 1,2-ethanediol catalyzed by sulfuric acid charring and the formation of tars are observed which lead to some product losses [8]. Accordingly, 1,4-dioxane is mainly manufactured by dehydration and ring closure of diethylene glycol. Recently diethylene glycol cyclization in the presence of ionic liquids is also presented [13].

In this paper, dehydration of 1,2-ethanediol and 1,4-butanediol is investigated to determine the role of AILs structure and molar ratio on the quality and yield of 1,4-dioxane and THF. The following AILs containing an alkane sulfonic acid group covalently bonded to pyridine and imidazole-containing cations are used: 1-sulfopropylpyridinium hydrogen sulfate [PyPS] [HSO_4], 1-sulfopropylpyridinium dihydrogen phosphate [PyPS] [H_2PO_4], 1-sulfopropylpyridinium *p*-toluenesulfonate [PyPS] [TsO], 1-methyl-3-(3-sulfopropyl)imidazolium hydrogen sulfate [MeImPS] [HSO_4], 1-methyl-3-(3-sulfopropyl)imidazolium dihydrogen phosphate [MeImPS] [H_2PO_4], 1-methyl-3-(3-sulfopropyl)-imidazolium *p*-toluenesulfonate [MeImPS] [TsO], 1-butyl-(3-sulfopropyl)imidazolium hydrogen sulfate [BuImPS] [HSO_4], 1-butyl-(3- sulfopropyl)imidazolium dihydrogen phosphate [BuImPS] [H_2PO_4], 1-butyl-(3-sulfopropyl)imidazolium *p*-toluenesulfonate [BuImPS] [OTs].

EXPERIMENTAL

AILs are prepared in two-step synthesis according to the method described in literature [7, 14]. On the first step N-alkylimidazoles are treated with equimolar amounts of 1,3-propanesultone. The mixture is stirred and heated for 24 hours at 60 °C using toluene as solvent. After cooling the obtained white crystals are washed with hot ethanol and dried for 2 h under vacuum (~2 Torr) at 100 °C. Purity of these salts is determined using HPLC/MS (*Waters Alliance* 2690 instrument, column 2,1×150 mm: stationary phase Atlantis®HILIC Silica, particle size 3 µm, mobile phase 10% H_2O, 90% methanol). 3-(1-Pyridinio)-1-propanesulfonate (commercially obtained from *Sigma–Aldrich*) and prepared imidazolium salts, with purity above 97%, are treated with equimolar amounts of corresponding acids: H_2SO_4 (95%, aqueous), H_3PO_4 (85%, aqueous) and *p*-toluenesulfonic acid monohydrate by heating reaction mixture for 24 h at 80 °C. Cooled products are washed by boiling with dried toluene with following evaporation and drying for 2 h under vacuum (~2 Torr) at 100 °C. The purity of prepared AILs is also tested with HPLC/MS, and AILs with purity above 97% are used for further reactions.

The dehydration of 1,2-ethanediol is carried out in the traditional distillation apparatus and the receiver is cooled with ice water. The mixture of AIL and 1,2-ethanediol is heated in an oil bath and the product is distilled off together with water. To remove water, the product is salted out with dried potassium carbonate. The dehydration of diethylene glycol and 1,4-butanediol is carried out in the same manner. The reaction products are analyzed with GC/MS (*Hewlett Packard HP 6890).* The water residues are determined with Karl–Fisher titrator (*836 Titrando Metrohm*). Water content in prepared ethers does not exceed 2%.

For the continuous distillation of 1,4-dioxane and THF the mixture of the AIL and the corresponding diol is heated in a distillation apparatus; when approximately 3/4 of product are collected the additional portion of diol is added dropwise. The collected products are treated and analyzed as mentioned above.

RESULTS

To evaluate the catalytic properties of sulfopropyl group-containing AILs, the dehydration of 1,2-ethanediol in [PyPS] [HSO_4] is investigated under different conditions. The reaction is carried out using different molar ratio of ionic liquid [PyPS] [HSO_4] to 1,2-ethanediol – 1:2, 1:10 and 1:20. The reaction is allowed to proceed at 150–160 °C and 1,4-dioxane is distilled off as soon as it forms. The results are presented in the Table 1. Reaction time indicates the finish of distillate formation.

The optimal yield of 1,4-dioxane (70%) and purity (95%) are obtained with the molar ratio of reagents equal to 1:10. The significant increase in reaction yield under reduced pressure is not observed. The dehydration time of 1,2-ethanediol is 3–5 hours; in comparison, for diethylene glycol it is around 2 hours, that corresponds to previously described results of diethylene glycol dehydration in ionic liquid [13]. The purity of all samples is above 90%, and the only impurity identified using GC/MS in all samples is 2-methyl-1,3-dioxolane, which is identified also in the products of cyclodehydration of diethylene glycol [8, 13]. The obtained yield of 1,4-dioxane without AIL in the presence of sulfuric acid is slightly lower (48%) but its purity is high; the yield of the product using the corresponding method in literature is 59% [12].

Table 1. **Preparation of 1,4-dioxane in ionic liquid [PyPS] $[HSO_4]$**

Molar ratio, [PyPS] $[HSO_4]$: 1,2-ethanediol[a]	Reaction time, h	T, °C	Yield, %	Purity determined by GC/MS, %
1:2	3	160	48	95
1:10	5	160	70	95
1: 20	5	160	60	90
1:10 (400 Torr)	5	150	62	94
1:10[b]	2	160	68	97
1:10[c]	3	160	48	96

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[a] The amount of diol is 0.1 mol.

[b] Diethylene glycol is used instead of 1,2-ethanediol.

[c] Sulfuric acid (95%) is used instead of [PyPS] $[HSO_4]$ [12].

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Hydrogen sulfate, dihydrogen phosphate and *p*-toluenesulfonate of pyridinium and imidazolium ionic liquids are tested to determine the effect of ionic liquid structure on the dehydration of 1,2-ethanediol. Results presented in the Table 2 show that the catalytic activity of AILs depends on their structure and the obtained yields of 1,4-dioxane are in the range between 20% (in [MeImPS] $[H_2PO_4]$) and 71% (in [MeImPS] $[HSO_4]$). Ionic liquids containing $[HSO_4]^-$ anion provide the highest yields and the products with purity – around 95%.

Table 2. **Synthesis of 1,4-dioxane in various AILs[a]**

AIL	Molar ratio AIL : 1,2-ethanediol	Reaction time, h	Yield, %	Purity determined by GC/MS, %
[BuImPS] $[HSO_4]$	1:10	5	63	95
[BuImPS] $[H_2PO_4]$	1:10	14	36	82
[BuImPS] [OTs]	1:10	14	62	92
[PyPS] $[HSO_4]$	1:10	5	70	95
[PyPS] $[H_2PO_4]$	1:10	>14	49	84
[PyPS] [TsO]	1:10	11	61	92
[MeImPS] $[HSO_4]$	1:10	5	71	94
[MeImPS] $[H_2PO_4]$	1:10	12	20	72
[MeImPS] [TsO]	1:10	13	42	90
[BuImPS] $[HSO_4]$	1:20	8	66	92
[PyPS] $[HSO_4]$	1:20	5	60	90
[MeImPS] $[HSO_4]$	1:20	7	63	95

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[a] Reaction temperature 160 °C, molar ratio of AILs to 1,2-ethanediol is 1:10, (the amount of diol is 0.1 mol).

The results of 1,2-ethanediol dehydration in AILs containing $[TsO]^-$ anion are similar to the results characteristic of ionic liquids containing $[HSO_4]^-$ anion, only the reaction time is longer.

$[H_2PO_4]^-$ anion containing AILs are less active catalysts because the distillation proceeds slowly and purity and yield of 1,4-dioxane are significantly lower than in the presence of AILs containing $[HSO_4]^-$ or $[TsO]^-$ anion. The observed difference could be explained with the impact of anion on the relative acidity of AILs. The Hammett function (H_o), that can be regarded as relative acidity of ionic liquids containing [PyPS], varies depending on the acid used for the AILs preparation: [PyPS] $[HSO_4]$ – $H_o = (–3.3)$; [PyPS] [TsO] – $H_o = (–2.0)$; [PyPS] $[H_2PO_4]$ – $H_o = (–1.5)$, determined using the Hammett method with UV-VIS spectroscopy [14]. Content of [PyPS]-containing ionic liquids and their acidity has an impact not only on the yield and purity of the dehydration product, but also on the 1,2-ethanediol dehydration reaction rate – time needed for the complete collection of distillate. The same tendencies have been observed also in imidazolium-based ionic liquids (Table 2). The structure of the investigated AILs cation has a negligible influence on the results of dehydration of 1,2-ethanediol. Such an influence is found in reactions of AILs with $[HSO_4]^-$ in the molar ratio of reagents equal to 1:20. The results are only slightly lower than those obtained when the molar ratio of reagents is 1:10. This fact also approves the catalytic activity of AILs in the reaction. The formation of one by-product – 2-methyl-1,3-dioxolane is observed in all samples of 1,4-dioxane apart from the applied pyridinium or imidazolium AILs.

To determine the reusability of AILs as catalysts in the dehydration reaction of 1,2-ethanediol, the reaction is repeated three times applying [BuImPS] $[HSO_4]$, the molar ratio of AIL to 1,2-ethanediol being 1:10. As the ionic liquid has changed its colour after reaction it is purified and dried in vacuum after the each cycle. Traditionally, three to five cycles are used to demonstrate the effectiveness of the ionic liquid [5, 13]. [BuImPS] $[HSO_4]$ maintains its catalytic activity as a minimum in three cycles of dehydration (Table 3). After the third cycle of 1,2-ethanediol dehydration, purification of the AIL is inconvenient due to its foaming and obvious presence of tars, that could be an indicator of the presence of some polyethylene glycols, identified as by-products in diethylene glycol dehydration in the presence of acid catalysts [8].

Table 3. **Results of 1,4-dioxane synthesis in the recycled [BuImPS] $[HSO_4]$**

Cycle Nr.	Purity determined by GC/MS, %	Yield, %
1	95	63
2	94	68
3	93	67

The final analyses of all 1,2-ethanediol cyclodehydration results lead to conclusion that hydrogen sulfate-containing acidic ionic liquids are most effective in the formation of 1,4-dioxane. The same tendency can be observed in cyclodehydration of 1,4-butanediol to THF in various anion-containing [PyPS]-based ionic liquids. Results are presented in the Table 4.

Table 4. **Results of THF syntheses from 1,4-butanediol in the various [PyPS]-containing ionic liquids**

AIL	Molar ratio AIL:1,4-butanediol	Reaction time[a], h	T, °C	Yield[b] , %
[PyPS] [HSO_4]	1:2	1	100	76
[PyPS] [HSO_4]	1:2	1	100	76
[PyPS] [HSO_4]	1:10	7	100	67
[PyPS] [HSO_4]	1:20	10	100	76
[PyPS] [HSO_4]	1:2	~ 0.2	140	70
[PyPS] [HSO_4]	1:10	~ 0.2	140	96
[PyPS] [HSO_4]	1:20	~ 0.5	140	96
[PyPS] [TsO]	1:10	~ 0,5	140	95
[PyPS] [TsO]	1:20	1	140	90
[PyPS] [H_2PO_4]	1:10	7	140	81
[PyPS] [H_2PO_4]	1:20	10	140	61

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[a] In all experiments the amount of 1,4-butanediol is 0.033 mol.

[b] The yield of THF after removing water with K_2CO_3, only THF is identified by GC/MS in all samples.

Cyclization of 1,4-butanediol in the presence of mineral acids proceeds at the temperatures above 100 °C [10]. For the reaction in [PyPS] [HSO_4], two temperatures are tested and the reaction at 140 °C is determined to proceed significantly faster than at 100 °C and it is completed in less than half an hour (see Table 4). Distillation of product starts immediately after warming up the reaction mixture. All the obtained products possess high purity determined by GC/MS and are characterized by high yields of THF. If the molar ratio [PyPS] [HSO_4]:1,4-butanediol equals to 1:2, distillation could be bothered due to viscosity of ionic liquid and rather small amount of the target product. After the reaction ionic liquid is only slightly changed in the colour and therefore it is used to determine the productivity and reusability of catalyst for continued distillation without purification of AIL after each cycle.

Table 5. **Results of dehydration of diols in continuous distillation process using AIL – [PyPS] [HSO_4][a]**

Diol	Product	Final total molar ratio [PyPS] [HSO_4]:diol[b]	T, °C	Yield, %	Purity determined by GC/MS, %
1,4-butanediol	THF	1:160	140	94	99
1,2-ethanediol	1,4-dioxane	1:40	160	37	87

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[a] Reaction time is ~ 8 hours, amount of AIL is 0.004 mol.

[b] In the beginning of reaction molar ratio [PyPS] [HSO_4] : diol is 1:20.

During 8 hours eight (starting) portions of 1,4-butanediol are added to the ionic liquid to guarantee the continuous distillation and only two portions of 1,2-ethanediol are managed. After reaction the purity and yield of THF are significantly higher in comparison with those of 1,4-dioxane, what corresponds to the reaction rates observed in the previous experiments.

CONCLUSIONS

In the cyclodehydration reaction of 1,2-ethanediol using acidic ionic liquids as the catalysts, 1,4-dioxane is formed. The yield and purity of reaction product are found to depend on the structure of acidic ionic liquid. In pyridinium- and imidazolium-based acidic ionic liquids containing hydrogen sulfate anion: [BuImPS] [HSO_4], [PyPS] [HSO_4], [MeImPS] [HSO_4], yields of 1,4-dioxane are higher than in ionic liquids containing $[TsO]^-$ and $[H_2PO_4]^-$ anion. In all samples of 1,4-dioxane, the presence of by-product 2-methyl-1,3-dioxolane is observed using GC/MS analyses.

Cyclodehydration of 1,4-butanediol in the presence of AILs proceeds faster, with higher yields than cyclodehydration of 1,2-ethanediol, that corresponds to the results obtained in the presence of mineral acids.

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DIOLU CIKLODEHIDRATĀCIJA SKĀBOS JONU ŠĶIDRUMOS

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KOPSAVILKUMS

Sulfoskābes grupu saturošo Brensteda skābo jonu šķidrumu vidē pētītas 1,2-etāndiola un 1,4-butāndiola ciklodehidratācijas reakcijas. Noskaidrota jonu šķidrumu struktūras un katalītiskās aktivitātes ietekme uz attiecīgo ciklisko ēteru – 1,4-dioksāna un tetrahidrofurāna – veidošanos.

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