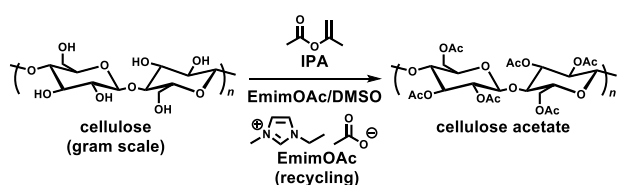


Polymer reaction of cellulose in ionic liquids as catalysts

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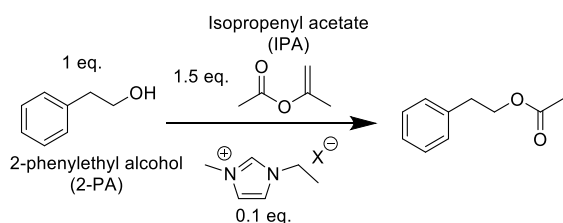
We recently reported that an ionic liquid 1-ethyl-3-methyl imidazolium acetate (EmimOAc) can serve not only as a cellulose solvent but also an activating reagent for transesterification reaction of OH groups in cellulose (Scheme 1)¹. However a mechanism of catalytic aspect of EmimOAc was not clear. The catalytic role of EmimOAc has been proposed to be owing to 1) the spontaneous generation of N-heterocyclic carbenes (NHCs) from imidazolium cation or 2) cooperative molecular recognition by either anions of EmimOAc. Herein, we investigate mechanistic insight of the role of EmimOAc in the transesterification reaction of cellulose by using several newly synthesized ionic liquids.



Scheme 1. Transesterification reaction of cellulose in EmimOAc with DMSO as a co-solvent.

In order to monitor the reactions in detail and provide a precise insight into the reaction mechanism, model reactions were carried out in EmimOAc, which employed simple reactants, 2-phenylethyl alcohol (2-PA) as a nucleophile and IPA as an ester donating reagent. First of all, the effect of anions was investigated (Table 1). As clearly shown, weakly basic anions were revealed to lose their organocatalytic properties. This has clearly reflected that the anion basicity played a crucial role in the organocatalytic properties of imidazolium ionic liquids.

Table 1. An effect of counter-anion structures on the TER of 2-PA and isopropenyl acetate catalyzed by 1-ethyl-3-methyl imidazolium ionic liquids with diverse counter-anions.

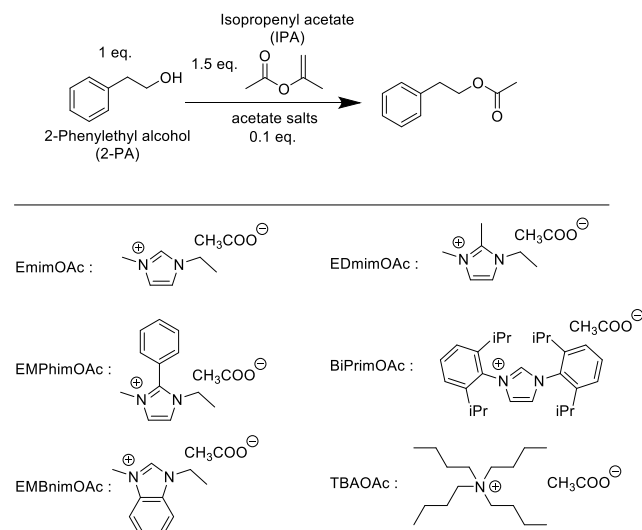


run	anion	pK _a	conv. (%)
1	CH ₃ COO ⁻	12.3	63.1
2	Cl ⁻	1.8	1.3
3	Br ⁻	0.9	1.0
4	CF ₃ COO ⁻	3.45	1.8

The key question we tackled is whether or not carbene species plays a crucial catalytic role in the transesterification processes. The proton at the C-2 position of imidazolium cations is rather acidic, so that its transfer to a base – if it occurs – generates carbene. It is widely conjectured that carbene thus produced participates directly in many reactions in Im-ILs featuring basic anions such as acetate. However, this is controversial in that NHCs have not been detected experimentally in many neat Im-ILs. Furthermore, according to a recent theoretical work on CO₂ capture, the generation of NHC from EmimOAc is highly unlikely in a polar environment due to NHC's instability.

In Table 2, the results for a model reaction of 2-phenylethyl alcohol in ionic liquids with several different cations are summarized. Because the model reaction proceeded even in ionic liquids EmPhimOAc and TBAOAc, in which carbene cannot be produced, these results suggested that it is not necessary to assume the presence of carbene to perform the reaction. Instead of the carbene, we will show a role of acetate anion in the reaction.

Table 2. An effect of cation structures on the transesterification reaction of 2-PA.



run	Employed salts	Conv. ^b
1	EmimOAc	63.1
5	BiPrimOAc	60.8
6	EMPhimOAc	22.1
7	EDMimOAc	29.1
8	EMBnimOAc	49.1
9	TBAOAc	27.0