Highly Efficient Epoxidation of Allylic Alcohols with Hydrogen Peroxide Catalyzed by Peroxometalate-Based Ionic Liquids

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Abstract: The peroxometalate anion-based ILs are prepared and characterized fully by the various methods. They have been used as efficient catalysts for the epoxidation of allylic alcohols under solvent-free and ice bath conditions. It was found that the parent anions of the ILs underwent structural changes after reaction with H_2O_2. Furthermore, the studies on catalytic activity, kinetics and $^1H(^{13}C)$ NMR and DTF calculation suggest that a hydrogen-bond interaction between peroxotantalate anion and hydroxyl group of allylic alcohols results in the high catalytic activity.

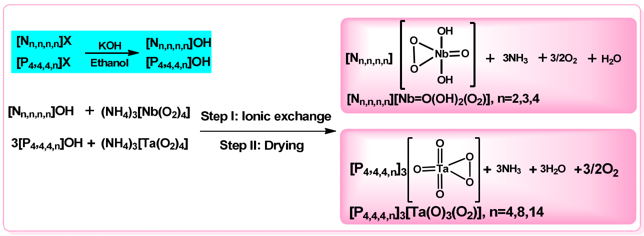
Keywords: Peroxoniobate/Peroxotantalate, Ionic Liquid, Epoxidation, Hydrogen Bonding

1. Introduction (11-point boldface)

Epoxidation of olefins and allylic alcohols is an important reaction in organic synthesis because the epoxy compounds are a type of important reaction intermediates, for example in the manufacture of polyether, β-haloalcohol, glycols, surfactants, etc.[1] The use of H_2O_2 as an oxidant is much more promising from economic and environmental points of view as only by-product (H_2O) is environmentally benign. In this work, we have developed a new series of novel ILs consisting of quaternary phosphonium/quaternary ammonium cations and a monomeric peroxoniobate/ peroxotantalate anion, which offered not only an efficient catalyst but also an approach of clear separation in epoxidation reaction[2].

2. Experimental (or Theoretical)

A series of peroxoniobate/peroxotantalate-based ionic liquids have been synthesized by ionic exchange. The synthetic route was shown in Scheme 1. The as-synthesized peroxotantalate salts have been characterized accordingly by NMR, TGA, FT-IR, Raman, HRMS, elemental analysis and ICP-AES analysis.

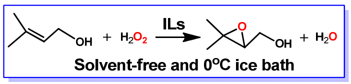


Scheme 1. The synthetic route of peroxometalate-based ILs.

3. Results and discussion

The studies revealed the parent anions of these ILs ($[N_{n,n,n,n}][Nb{=}O(O_2)(OH)_2]$, $N_{n,n,n,n}$= quaternaryammonium cation; $[P_{4,4,4,n}]_3[Ta(O)_3(O_2)]$, $P_{4,4,4,n}$=quaternary phosphonium cation) underwent structural transformation in the presence of excess of H_2O_2. The forming active species exhibited excellent catalytic activity as the turnover frequency reached up to 285 h^{-1} and satisfactory recyclability in the epoxidation of various allylic alcohols under very mild conditions by using only one equivalent of hydrogen peroxide as an oxidant. The NMR and DFT studies showed the reaction was facilitated through a hydrogen bonding mechanism, in which the peroxo group (O-O) of peroxometalate anion served as the hydrogen bond acceptor and hydroxyl group in allylic alcohols served as hydrogen bond donor. This work demonstrated that simple monomeric peroxometalate can catalyze epoxidation of allylic alcohol (3-methyl-2-buten-1-ol) efficiently under very mild conditions (Table 1). This IL catalyst system can be easily extended to the epoxidation of a wide scope of allylic alcohols[3,4].

Table 1. Solvent-free epoxidation of 3-methyl-2-buten-1-ol with different catalysts.[a]



Entry	Catalysts	Con. /[%][c]	Sel. [%] epoxide	Sel. [%] diol	TOF/h^{-1}
1	$[P_{4,4,4,4}]_3[Ta(O)_3(O_2)]$	98.7	≥99	< 1	285
2	$[P_{4,4,4,8}]_3[Ta(O)_3(O_2)]$	96.8	≥99	< 1	265
3	$[P_{4,4,4,14}]_3[Ta(O)_3(O_2)]$	95.9	≥99	< 1	237
4	$[N_{3,3,3,3}][Nb{=}O(O_2)(OH)_2]$	96.4	≥99	< 1	219
5	$[N_{4,4,4,4}][Nb{=}O(O_2)(OH)_2]$	96.4	≥99	< 1	246
6	$[N_{6,6,6,6}][Nb{=}O(O_2)(OH)_2]$	97.1	≥99	<1	295

[a] Reaction conditions: 2 mmol of 3-methyl-2-buten-1-ol, 2 mmol of 30%, aqueous H_2O_2, 0.05 mmol of the catalyst, T=0°C, t=1.5 h, solvent free. Conversion determined by using GC with dodecane as an internal standard.

Taking ionic liquid $[P_{4,4,4,n}]_3[Ta(O)_3(O_2)]$ as an example, a hydrogen bonding mechanism has been suggested in the allylic alcohol epoxidation (Figure 1). In this reaction process, an intermolecular oxygen transfer process could be assisted, already at the start of the reaction and even more so in the transition state by a hydrogen-bonding interaction, where peroxo group (O-O) could serve as the hydrogen bond acceptor and allylic hydroxyl group (-OH) served as hydrogen bond donor. Hydrogen bonding could alter deeply the transition-state structure geometry observed in the epoxidation of allylic alcohol, and this could facilitate active oxygen of peroxo group to transfer to double bond to get corresponding products.

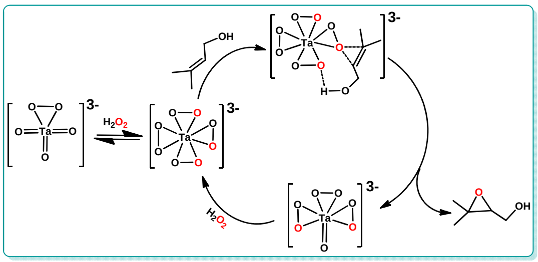


Figure 1. Proposed mechanism for epoxidation of allylic alcohols with H_2O_2 catalyzed by the monomeric peroxotantalate anion-functionalized ILs.

4. Conclusions

This work demonstrated the first example of ILs based on monomeric peroxoniobate and peroxotantalate anions with a deep insight into the evolution of the active center in the course of epoxidation reaction. In the present catalytic system, there is not a direct coordination interaction between the substrate molecules and the metal site and the catalytic reaction proceeded via the hydrogen bonding interaction mechanism, where the peroxide species around metal site can be transformed reversibly. This implied that the structure of the catalytically active anions is regenerated easily. We envisage that these ionic liquids provided a new approach to oxidation catalysis and their application to catalysis will be extended in the future work.

References

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