

Ionic liquids and supercritical carbon dioxide as solvents for NHPI-catalysed oxidation reactions

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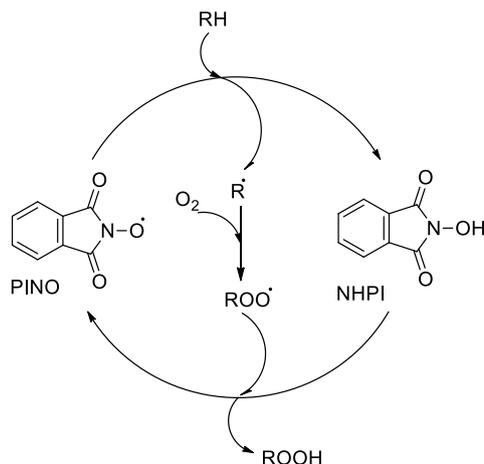
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Abstract – Studies on the possibility of application of ionic liquids or $scCO_2$ as solvents in hydrocarbons oxidation with oxygen in the presence of *N*-hydroxyphthalimide have been reported. Various alkylaromatics (cumene, ethylbenzene, mono- and diisopropyl naphthalene, mono- and diisopropylbiphenyl) and α -methylstyrene were used as starting materials.

Keywords – oxidation, *N*-hydroxyphthalimide, ionic liquids, supercritical CO_2 , cumene, α -methylstyrene

Introduction

The catalytic activity of *N*-hydroxyphthalimide (NHPI) in the oxidation of hydrocarbons with oxygen has been intensely studied [1-3]. The reaction proceeds via a free radical mechanism. PINO radical is formed from NHPI and abstracts the hydrogen atom from oxidized hydrocarbons (Scheme 1). PINO formation is often accelerated by addition of transition metal compounds, azo-initiators or aldehydes as co-catalysts. The catalytic activity of NHPI has been demonstrated in several processes, including cumene, ethylbenzene, toluene, cyclohexane, α -methylstyrene oxidations [1-3].



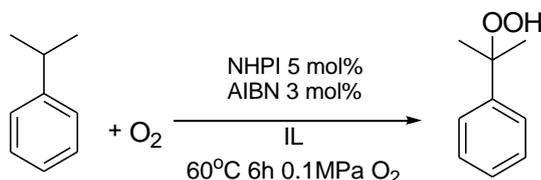
Scheme 1. Mechanism of NHPI-catalysed hydrocarbons oxidation [1-3]

NHPI has attracted considerable interest because of high activity as well as it is non-toxic and can be easily prepared from phthalic anhydride and hydroxylamine. However, due to its low solubility in hydrocarbons, most often NHPI-catalysed reactions are carried out in polar solvents such as acetic acid, acetonitrile, and benzonitrile. To eliminate or limit the amount of solvent, lipophilic derivatives of NHPI were applied [4]. Additionally, a few attempts have been undertaken to use ionic liquids (ILs) or supercritical carbon dioxide ($scCO_2$) in place of organic solvents. Advantages of ILs include low volatility, high polarity and chemical and thermal stability. Usage of CO_2 as a solvent is very promising because it is not toxic, its critical parameters are mild (304.2 K, 7.38 MPa), can be easily separated from a post-reaction mixture and it does not undergo subsequent oxidation reaction.

Results

NHPI-catalysed oxidation reactions in ILs

ILs composed of 1-alkyl-3-methylimidazolium cations (alkyl: ethyl [emim], butyl [bmim], hexyl [hmim], octyl [omim]) and [BF₄], [PF₆], [NTf₂], [CF₃SO₃], [O_cOSO₃] and [CH₃OSO₃] as anions were used as solvents in the oxidation of cumene with oxygen using NHPI as a catalyst (scheme 2) [5].

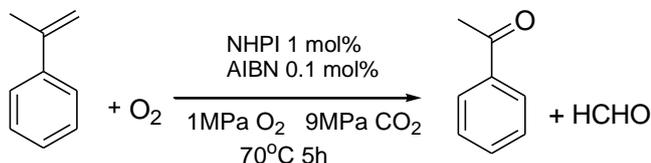


Scheme 2. NHPI-catalysed cumene oxidation in ILs [5]

High conversion of cumene (36.4%) and selectivity to hydroperoxide (100%) were obtained in [bmim][NTf₂]. The cumene conversion obtained in this IL was lower than those obtained in the classical polar organic solvent benzonitrile (56,7%), but higher than obtained in *tert*-butylbenzene (10.5%). [bmim][NTf₂] is characterized by good oxygen solubility, low viscosity as well as does not accelerate hydroperoxide decomposition. It was also demonstrated that high conversions and selectivities to appropriate hydroperoxides were obtained when [bmim][NTf₂] was applied as a solvent in NHPI-catalysed oxidation of other isopropyl aromatic hydrocarbons (mono- and diisopropyl naphthalene, mono- and diisopropyl biphenyl) and ethylbenzene with oxygen.

NHPI-catalysed oxidation reactions in scCO₂

NHPI-catalysed oxidative cleavage reaction of α -methylstyrene with oxygen in scCO₂ was studied [6].



Scheme 3. NHPI-catalysed oxidation of α -methylstyrene in scCO₂ [6]

When oxidation of α -methylstyrene was performed under pressure of oxygen (0.5 MPa) conversion of 82% and selectivity to acetophenone of 62% were achieved. When scCO₂ was used conversion of α -methylstyrene decreased to 52%, but acetophenone selectivity increased to 74% (scheme 3).

References

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