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# Cobalt/N-Hydroxyphthalimide(NHPI)-Catalyzed Aerobic Oxidation of Hydrocarbons with Ionic Liquid Additive

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## ABSTRACT

A highly efficient and solvent-free system of cobalt/NHPI-catalyzed aerobic oxidation of hydrocarbons was developed using imidazolium-based ionic liquid (IL) as an additive. These amphipathic ILs were found self-assemble at the interface between the organic hydrocarbons and the aqueous phase of catalyst combination (Co/NHPI), with forming a solution of reversed multilamellar vesicles for catalysis. The initial reaction rate was influenced by both the composition of microdomains and the structure of IL launched. Consequently, a proper water content ($\chi_{H2O}$) of wet IL was requisite to reach the optimum reactivity. Besides, the interfacial boundary between aqueous and organic phase composed by C2-alkylated imidazolium ILs, such as [bdmim]$SbF_6$ and [$C_{12}$dmim]$SbF_6$, not only has ternary aggregates (hydrocarbons/IL/$H_2O$) of higher stability but renders $O_2$ a faster diffusion rate and higher concentration, thereby offering a high reactivity of the protocol towards hydrocarbon oxidation.

## 1. Introduction

Aerobic oxidation and functionalization of hydrocarbons is a promising subject in industrial chemistry [1]. Many fundamental chemicals such as terephthalic acid [2], KA oil (a mixture of cyclohexanone and cyclohexanol) [3], phenol accompanied by acetone [4], benzoic acid [5], are produced by homogeneous liquid-phase oxidations with $O_2$ as the external oxidant. However, hydrocarbon oxidations suffer a major limitation imposed by their intrinsic nature: the reaction products are generally more reactive than the starting precursors [6]. In the past two decades, many endeavours had been put to explore novel strategies with better selectivity under milder reaction conditions. Consequently, homogeneous catalysis includes transition-metal [7], dye-related [8], enzymatic [9], biomimetic [10], and halogen-based [11] catalysis were developed. Pioneered by Grochowski's group, N-hydroxyphthalimide (NHPI) was recognized as a mediator for free-radical reactions [12]. In 1995, Ishii and co-workers reported alkanes and alcohols could be effectively oxidized to the corresponding carbonyl compounds, which opened up a history of hydrocarbon oxidations catalyzed by NHPI [13]. Since then, a combination of NHPI with either transition metal salts [14] or various non-metal co-catalysts [15] was successively employed to accelerate the autoxidation efficiency. However, NHPI as a catalyst suffers two major shortcomings of low solubility in nonpolar organic medium and low thermo stability [16]. To address this issue, the focus was turned to the molecular design of novel structures of nitroxyl radical precursor with increased lipophilicity and stability [17]. It's also requisite to render the O—H group thereof proper bond dissociation energy (BDE) for the high reactivity towards hydrocarbons [18]. Alternatively, the search for new reaction medium as solvent/phase transfer catalyst (PTC) was also effective and attracted attentions [19].

Ionic liquids (ILs) were initially introduced as alternative green reaction medium because of their unique chemical and physical properties, such as nonvolatility, nonflammability, thermal stability and controlled miscibility [20]. Quite a lot of aerobic oxidations were examined in ILs, which exhibited enhanced activities as compared with that in the conventional organic solvents [21]. In such a system, ILs cannot be considered inert since the formation and transfer rate of radical species generated in situ should be strongly affected by the

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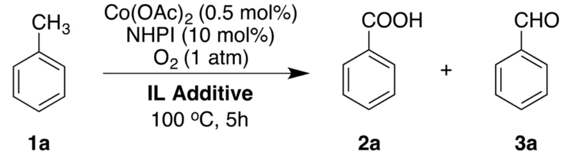
presence of an ionic environment. Noteworthy, mechanistic studies of autoxidation in the presence of NHPI and cobalt salt demonstrated both regeneration of nitroxyl radicals and addition of $O_2$ to carbon radical are diffusion-controlled process [16b]. Consequently, there should be pronounced solvent effect on the reaction efficiency if IL solution was launched. Closely related, Compton and coworkers conducted systematic researches on the electron reduction of oxygen ($O_2$) in a series of ILs [22]. The diffusion rate of $O_2$ and $O_2\cdot^-$ were found strongly depend on the specific structure of ILs using ultramicroelectrode (UME) technology. Besides, the micelles or higher aggregates presented in IL or multicomponent system containing IL have been recognized [23], wherein the distribution of substrates and transiency species could be designed to reach high reaction efficiency. For instance, the extensively explored binary system of IL/$H_2O$ was recently launched in the aerobic oxidative transformation of aliphatic alcohols to carbonyl compounds [24]. The high efficiency obtained was attributed to the local concentration experienced by the reactants in the assembly is higher than in a bulk solution. Finally, from a viewpoint of molecular level, functionalization of ILs with hydrogen-bonding donor (HBD) groups was supposed beneficial to accelerate electron transfer rate from metal complexes to the oxygen molecule ($O_2$), a requisite step in the initial stage of metal-catalyzed aerobic oxidation. Evidently, Jacobsen [25] and Song [26] disclosed imidazolium-based ILs exhibited a dramatic acceleration effect on the electron transfer from metal complexes to $O_2$, which was ascribed to the stabilization of the oxygen radical anions ($O_2\cdot^-$) by coordinating with the acidic C2-H of imidazolium-based ILs. We, therefore, envisioned the efficiency of Co/NHPI-catalyzed aerobic oxidation of hydrocarbons could be effectively tuned by using different IL as an additive or solvent medium. The readily modified structure of ILs may render it possible to explore the important structure-performance relationship therein.

## 2. Results and discussion

We started with screening various imidazolium-based ILs as an additive to the Co/NHPI catalytic system for the aerobic oxidation of toluene (**1a**) (Table 1, entries 1–8). Notably, moisture content in each wet IL ($\chi_{H2O} = n_{H2O}/n_{IL}$) under study was controlled less than $4.8 \times 10^{-2}$ determined by Karl Fischer titration. In addition, the performance in general media, like acetic acid (HAc) [27], was also studied for comparison (entries 9–11). All oxidations were carried out in the presence of $Co(OAc)_2$ (0.5 mol%) and NHPI (10 mol%) under $O_2$ (1 atm) at 100 °C for 15 h, with generating benzoic acid (**2a**) as the major product together with traces of benzaldehyde (**3a**). As indicated by entries 1–4, the reaction efficiency decreases with an increasing acidity of C2 − H in the imidazolium cation, albeit with distinction being far less than we expected. The relatively higher yield of **2a** obtained in the presence of [bmim]Br ([bmim]: butyl metylimidazolium) (entry 5) is likely attributed to the cooperative role of $Br^-$ in the cobalt-catalyzed aerobic oxidation [28]. The imidazolium cation was then functionalized with stronger HBD groups such as carboxylic acid with the aim to further optimize the oxidation efficiency through accelerating the electron transfer rate from Co(II) to $O_2$. Unfortunately, the corresponding reaction proceeded sluggishly (entry 6), with leading to an overall yield of products upon oxidation in less than 34%. Instead, significant improvements were obtained when C2 − H was blocked with an alkyl group (entries 7 and 8). Besides, it is beneficial to reach a relatively high yield of **2a** by introducing a longer carbon chain at N1-position. In comparison, the performance is poor in the presence of HAc (entry 10) as an additive. A comparable yield of **2a** could be attained in HAc when its amount was increased up to a solvent scale (5 mL, entry 10).

**Table 1**
Co/NHPI-catalyzed aerobic oxidation of toluene (**1a**) in the presence of imidazolium-based IL as an additive[a].



| Entry | Additive | Conv. (%) | Yield (%)[b] | |
|---|---|---|---|---|
| | | | 2a | 3a |
| 1 | $[bmim]SbF_6$ | 55 | 53 | 2 |
| 2 | $[bmim]PF_6$ | 52 | 50 | N.D.[c] |
| 3 | $[bmim]NTf_2$ | 49 | 47 | 2 |
| 4 | $[bmim]BF_4$ | 44 | 42 | 1 |
| 5 | [bmim]Br | 50 | 48 | 1 |
| 6 | $[HOOC_4mim]SbF_6$ | 34 | 32 | 1 |
| 7 | $[bdmim]SbF_6$ | 72 | 71 | 1 |
| 8 | $[C_{12}dmim]SbF_6$ | 80 | 78 | 1 |
| 9 | HAc | 56 | 54 | 1 |
| 10 | HAc[d] | 82 | 80 | 2 |

[a] Reaction condition: **1a** (2 mM), NHPI (10 mol%), $Co(OAc)_2$ (0.5 mol%), additive (5 mol%), $O_2$ (1 atm), 100 °C, 15 h.
[b] Yield determined by GC through using areas of peak normalization method.
[c] N.D.: not detected.
[d] Additive (5 mL). [bmim]: butyl metylimidazolium; [bdmim]: 3-butyl-1,2-dimethyl-1H-imidazol-3-ium; [$C_{12}$dmim]: 1-dodecyl-3,3-dimethylimidazolium; [$HOOC_4$mim]: 3-butyl-2-carboxy-1-methyl-1H-imidazol-3-ium.

The impact of catalyst species on the autoxidation rate of **1a** was subsequently studied by kinetic profiles of several experiments, using different catalyst combinations at 80 °C (Fig. 1). Evidently, the ternary Co/NHPI/$[C_{12}dmim]SbF_6$ ([$C_{12}$dmim] = 1-dodecyl-3, 3-dimethylimidazolium) (**b**) is more reactive than the dual combinations of either Co/$[C_{12}dmim]SbF_6$ (**d**) or NHPI/$[C_{12}dmim]SbF_6$ (**c**). In addition, we found it's requisite to attain high reaction efficiency through loading the wet IL of a proper $\chi_{H2O}$, despite the aerobic oxidation process thereof accompanied with production of $H_2O$. As it depicted, the oxidative conversion of **1a** to **2a** underwent apparently faster within 50 min when $\chi_{H2O}$ in $[C_{12}dmim]SbF_6$ was increased from ca. $5.5 \times 10^{-3}$ (**a**) to $7.7 \times 10^{-2}$ (**b**). On the other hand, the initial oxidation rate was slightly reduced when $\chi_{H2O}$ was increased up to $1.8 \times 10^{-1}$ (**e**).

We, therefore, can postulate these amphipathic ILs self-assemble at the interface between the apolar hydrocarbons, such as **1a**, and the aqueous phase of catalyst combination (Co/NHPI), with forming a solution of reversed multilamellar vesicles. In such a system, IL additive functions as a kind of surfactant or even phase transfer catalyst during the initial stage of oxidation. Consequently, the reaction activity was influenced by not only the composition of microdomains but also the

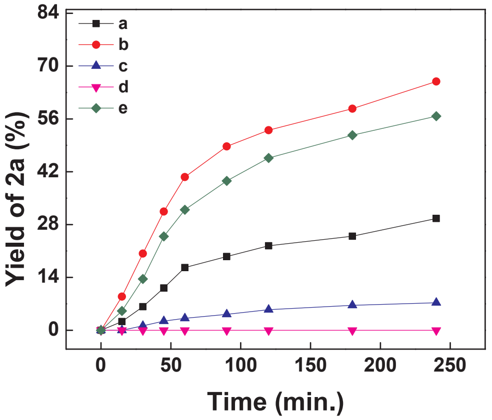


**Fig. 1.** Time-course plots for the aerobic oxidation of **1a** to **2a**. General conditions: **1a** (2 mmol), $O_2$ (1 atm), 80 °C; a) $Co(OAc)_2$ (1.0 mol%), NHPI (10 mol%), $[C_{12}dmim]SbF_6$ (5 mol%), $\chi_{H2O}$ ($5.5 \times 10^{-3}$); b) $Co(OAc)_2$ (1.0 mol%), NHPI (10 mol%), $[C_{12}dmim]SbF_6$ (5 mol%), $\chi_{H2O}$ ($7.7 \times 10^{-2}$); c) NHPI (10 mol%), $[C_{12}dmim]SbF_6$ (5 mol%), $\chi_{H2O}$ ($5.5 \times 10^{-3}$); d) $Co(OAc)_2$ (1.0 mol%), $[C_{12}dmim]SbF_6$ (5 mol%), $\chi_{H2O}$ ($5.5 \times 10^{-3}$); e) $Co(OAc)_2$ (1.0 mol%), NHPI (10 mol%), $[C_{12}dmim]SbF_6$ (5 mol%), $\chi_{H2O}$ ($1.8 \times 10^{-1}$).

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