The dramatic acceleration effect of imidazolium ionic liquids on electron transfer reactions†

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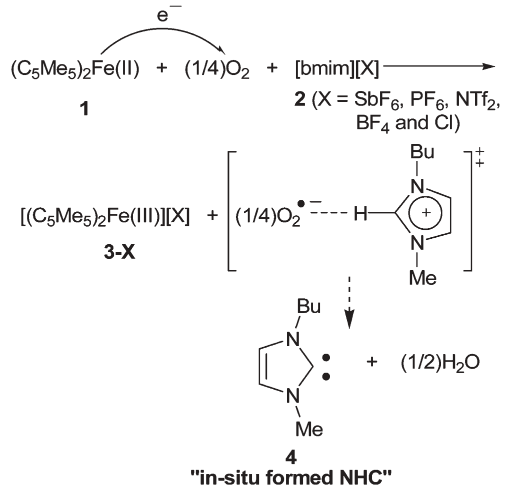
Imidazolium ionic liquids (ILs) exhibited a dramatic acceleration effect on the electron transfer from metal complexes such as $(C_5Me_5)_2$Fe(II) and $(C_5Me_5)_2$Co(II) to the oxygen molecule; this acceleration effect can be ascribed to the stabilization of the oxygen radical anions by coordinating with the acidic C2-H of imidazolium ILs.

In nature, electron transfer plays a fundamental role in most important processes such as photosynthesis, respiration and nitrogen fixation. Transition metals such as copper and iron are known to be crucial in electron transport as one-electron redox-active centers within proteins.[1] Mimicking these biological systems enables the aerobic oxidation of metal complexes, which are promoted by Brønsted and Lewis acids. Mechanistically these aerobic oxidations proceed through electron transfer from metal complexes to an oxygen molecule, thereby affording an oxygen radical anion intermediate, which can be stabilized by coordinating with an acid, consequently lowering the activation energy.[2] In this paper, we present our finding of the remarkable ability of imidazolium-based ionic liquids (ILs) to promote electron transfer reactions such as aerobic oxidation of metal complexes.

Imidazolium ILs have recently received a great deal of attention as potential new media for organic synthesis, catalyst support, and nanostructure construction materials.[3] The physicochemical properties of ILs such as hydrophilicity and hydrophobicity can easily be varied by changing the counter anions. We have recently demonstrated that the anion-directed, switchable properties of the ILs could be transferred to the self-assembled monolayer surfaces and carbon nanotubes.[4] During our on-going study on IL chemistry,[5] we expected, as depicted in Scheme 1, that the aerobic oxidation of a metal complex such as $(C_5Me_5)_2$Fe(II) (**1**) might also be promoted by employing imidazolium ILs since the imidazolium ring contains the acidic C2-proton,[6] for which the acidity scale largely depends on the degree of hydrogen bonding between C2-H and anion [X].[6b] The more basic anions such as Cl^- can be strongly coordinated to the C2-proton in the imidazolium cation *via* hydrogen bonding, thereby weakening the acidity of the imidazolium proton. Hence, it could be assumed that the rate of aerobic oxidation of metal complexes may be largely dependent on the counter anion of imidazolium ILs.

In order to investigate whether imidazolium ILs can really promote the one-electron transfer reaction, we first carried out the aerobic oxidation of Fe(II) complex **1** in the presence and absence of ILs **2** and the progress of the reaction was monitored periodically by UV-Vis spectroscopy. Upon mixing **1** (20 mg) with [bmim][X] **2** (9.2 mmol; bmim = 1-butyl-3-methylimidazolium cation; X = SbF_6, PF_6, NTf_2, BF_4 and Cl) in CH_2Cl_2 (10 mL), the color changed from yellow to green. As shown in the UV-Vis spectra in Fig. 1 (curve a–e), in the presence of [bmim][X] **2**, a strong red shift was observed in the specific absorption of Fe(II) complex **1** from 423 nm to 779 nm of Fe(III)-X **3** complex. In contrast to these results, no oxidation was observed in the absence of ILs **2** (curve f) indicating that IL presence is crucial for the aerobic oxidation of the metal complex. As expected, the oxidation rate was highly dependent on the anion's structure and thus decreased in the order of $SbF_6^- > PF_6^- > NTf_2^- \sim BF_4^- \gg Cl^-$ which reflected the relative acidity of the C2-H.

To confirm the role of acidity of the C2-proton of ILs **2** in the oxidation process, we also carried out the same oxidation of **1** (20 mg) in CH_2Cl_2 (10 mL) in the presence of three different types of SbF_6 salts (4.6 mmol),[7] *i.e.*, $[Bu_4N][SbF_6]$, **2**-SbF_6 and [*N*-butylthiazolium][SbF_6]. As anticipated, the oxidation-promoting effect profile of these salts was consistent with their relative acidity scale. Thus, in the presence of $[Bu_4N][SbF_6]$, which does not



Scheme 1 Proposed mechanism for aerobic oxidation of **1** to **3**-X promoted by imidazolium ILs **2**.

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† Electronic supplementary information (ESI) available: compound characterization data for **3**-SbF_6 (X-ray data) and *N*-butylthiazolium [SbF_6] (^{1}H-, ^{13}C- and ^{19}F-NMR) and UV-Vis spectra of a mixture of $(C_5Me_5)_2$Co with ILs. See DOI: 10.1039/b708044a

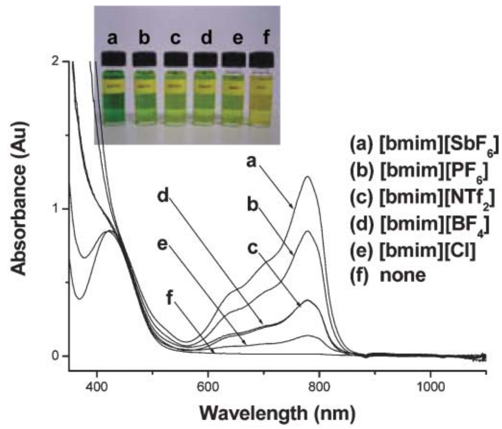


Fig. 1 UV-Vis spectra of a mixture of **1** (0.06 mmol) either with or without ILs **2** (9.2 mmol) in CH_2Cl_2 (10 mL) (after 1 h).

possess the Brønsted proton, the oxidation reaction proceeded sluggishly (curve c of Fig. 2), whereas, [*N*-butylthiazolium][SbF_6] which bears a more acidic proton than does **2**-SbF_6,[8] accelerated the oxidation rate more dramatically than did **2**-SbF_6 (compare curve a and b of Fig. 2). All these observations strongly support our contention that the formed oxygen radical anion can be stabilized by coordinating with the acidic C2-proton of the imidazolium ring, whereas such a stabilization effect is impossible in conventional solvents.

Following these encouraging results, we extended the IL-promoted electron transfer to other metallic system such as $(C_5Me_5)_2$Co(II) (**5**) to gain generality of this protocol. The aerobic oxidation of **5** in CH_2Cl_2 was carried out in the presence and absence of ILs ([*N*-butylthiazolium][SbF_6], **2**-PF_6, **2**-NTf_2 and **2**-OTf). As expected, in the presence of ILs, the dark-brown Co-complex **5** was rapidly oxidized to the yellow Co(III)-X complex. Moreover, similar to the case of Fe complex **1**, oxidation rate was dependent on the relative acidity of the C2-H of ILs ([*N*-butylthiazolium][SbF_6] > **2**-PF_6 > **2**-NTf_2 > **2**-OTf; UV-Vis spectra, see ESI†).

According to our proposed mechanism (Scheme 1), the aerobic oxidation of **1** promoted by imidazolium ILs **2** should afford Fe(III)-X **3** and the *in-situ* formation of *N*-heterocyclic carbene (NHC) **4** (or its derivatives). Thus, to obtain more direct evidence for the promoting ability of imidazolium ILs **2** for electron transfer reactions, we tried to isolate the oxidized Fe(III)-SbF_6 complex **3**-SbF_6. Fortunately, we could isolate green colored, single crystals of Fe(III)-SbF_6 complex **3**-SbF_6 by standing the reaction mixture of **1** and [bmim][SbF_6] in CH_2Cl_2 at room temperature for two weeks and identify its structure by single crystal X-ray crystallography (Fig. 3) (ESI†).[9] According to our aforementioned assumption, NHCs should also be formed *in situ* during the aerobic oxidation of **1** in the presence of ILs **2**. However, despite our intensive efforts, we failed to isolate and identify NHC and its derivatives. Therefore, to prove the *in-situ* NHC formation during the electron transfer reaction from **1** to oxygen in the presence of imidazolium ILs **2**, we carried out transesterification reaction under O_2 atmosphere, since nucleophilic NHCs are known to be efficient catalysts for this reaction.[10] For this experiment, benzyl alcohol (0.2 mL, 9.6 mmol), vinyl acetate (0.22 mL, 4.8 mmol), and 20 mol% (based on benzyl alcohol) of [bmim][SbF_6] were added to a flask loaded with 20 mol% of **1** (Scheme 2). The resulting green colored reaction mixture was then stirred under O_2 atmosphere at room temperature for 24 h. Surprisingly, the reaction proceeded smoothly and thus the acylated product (benzyl acetate) was isolated in about 50% yield, although the sterically non-hindered NHCs such as **4** may have been highly unstable. However, in the absence of ILs **2**, the same reaction barely occurred with a product yield of less than 2%. The results presented here combine to form strong evidence that imidazolium ILs **2** promoted the electron transfer reactions. It should also be here noted that the base-free generation of NHCs could also be possible through the aerobic oxidation of metal complex with the imidazolium ILs.[11]

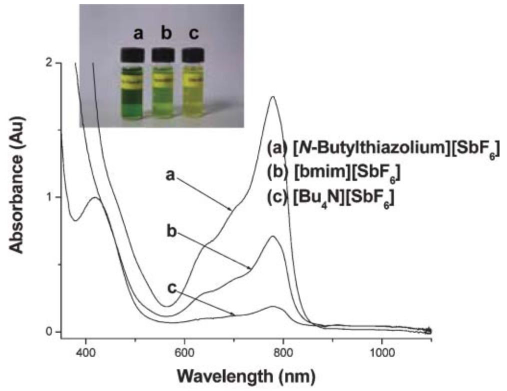


Fig. 2 UV-Vis spectra of a mixture of **1** (0.06 mmol) with a different type of SbF_6-salts (4.6 mmol) in CH_2Cl_2 (10 mL) (after 2 h).

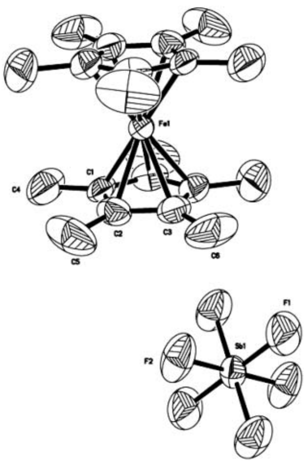
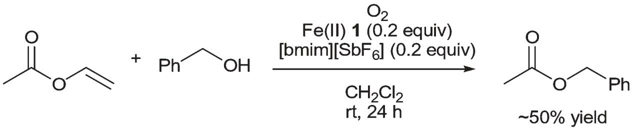


Fig. 3 Single X ray crystal structure of $(C_5Me_5)_2$Fe(III)-SbF_6 (**3**-SbF_6) with the 50% probability thermal ellipsoids.

In conclusion, the dramatic acceleration effect of imidazolium ILs on the electron transfer from metal complexes such as $(C_5Me_5)_2$Fe(II) (**1**) and $(C_5Me_5)_2$Co(II) (**5**) to oxygen molecule was found which can be ascribed to stabilization of the oxygen radical



Scheme 2 Transesterification catalyzed by base-free generated NHC.

anions by coordinating with the acidic C2-H of imidazolium ILs. Moreover, the oxidation rate can be controlled by simple switching of the IL anion. We expect the present results to open up many applications in the research area of electron transfer reactions. For example, specific catalytically active oxidation states of transition metal complexes can be stabilized in ILs against their reduction. Moreover, the aerobic oxidation of metal complexes promoted by imidazolium IL may be also utilized as a base-free generation method of N-heterocyclic carbenes able to catalyze many organic reactions.

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7 To compare the promoting effect of these salts on this oxidation more accurately, half the amounts (4.6 mmol) of salts were used as compared to those (9.2 mmol) used in Fig. 1. When the same amounts of salts were used as in Fig. 1, in the cases of **2**-SbF_6 and [*N*-butylthiazolium][SbF_6], the oxidations proceeded too fast and thus were completed within 1 h.

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11 To generate the NHCs from imadazolium salts, a strong base is usually needed which can cause side reactions.