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Oxidation of thiols with molecular oxygen catalyzed by cobalt(II) phthalocyanines in ionic liquid†

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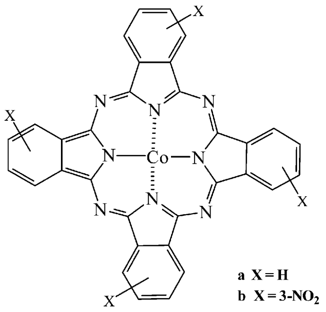
An efficient procedure for catalyst solubility, recycling and easy product isolation in oxidation of thiols to disulfides with molecular oxygen catalyzed by cobalt(II) phthalocyanines dissolved in ionic liquid at room temperature is reported.

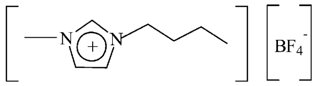
Phthalocyanines (Pcs) constitute a remarkably versatile and robust class of compounds with diverse technological applications.[1–4] Metallophthalocyanines have been used as efficient biomimetic catalysts for oxidation, reduction and other reactions of different organic compounds.[5] On the other hand, alkyl mercaptans and other sulfur containing impurities present in petroleum are major environmental pollutants. They are also corrosive and poisoners of different catalysts during the processing and purification of petroleum. Further, the oxidation of thiols to disulfides has also been involved in many synthetic, biological[6] and oil-sweetening processes.[7,8] The oxidation of thiols to disulfide has been achieved by molecular oxygen in basic aqueous H_2O_2 in the absence and presence of catalyst and with other oxidants under different reaction conditions.[9,10] Efficient oxidation of thiols to disulfides catalyzed by transition metal phthalocyanines in aqueous, water-in-oil and oil-in-water microemulsions has been reported by us and others.[11,12] However, the main drawbacks of these catalysts are the poor solubility in common organic solvents and the formation of μ-oxo-dimers in the case of water-soluble tetrasulfonated phthalocyanines which decrease the reactivity in aqueous media. Thus, metallophthalocyanines have been immobilized on a variety of solid supports for stability and easy catalyst recovery but these supported catalysts also often suffer from drawbacks such as lower activity than soluble catalysts due to either chemical or diffusional restrictions.[13,14]

The 1,3-dialkylimidazolium tetrafluoroborates [bmim][BF_4] are an important class of ionic liquids and they are environmentally benign solvents due to their unique chemical and physical properties such as excellent chemical and thermal stability with ease of reuse, miniscule vapour pressure, unique misibilities and non-flammability.[15,16] They behave macroscopically like polar aprotic solvents but are non-coordinating. They have been employed as solvents for many organic and enzymatic transformations,[17,18] in liquid–liquid separation[19] and recycling of organometallic catalysts.[20,21] Further, imidazolium cation containing ionic liquids have also been shown to enhance the rate of reaction with facilitation of easy catalyst recovery.[22] Herein, we report the oxidation of selected thiols to disulfides with molecular oxygen catalyzed by cobalt(II) phthalocyanines dissolved in imidazolium ionic liquid under mild reaction conditions.

The required cobalt(II) phthalocyanine [CoPc] (**1a**) and cobalt(II) tetranitrophthalocyanine [CoTNPc] (**1b**) were synthesized by a template method using phthalic anhydride or 3-nitrophthalic anhydride, urea and $CoCl_2$.†[9,23] The catalysts were purified by a reported procedure and their structures were confirmed by IR and UV-visible spectroscopic data. Catalysts **1a–b** were freely dissolved in [bmim][BF_4] (**2**) by simple mixing and the oxidation of different thiols was carried out in homogeneous medium under oxygen atmosphere (Fig. 1). A mixture of thiophenol and **1a** in **2** was stirred for 45 min in the presence of molecular oxygen to give diphenyl disulfide in 95% yield. Similarly, the oxidation of other thiols with molecular oxygen catalyzed by **1a** or **1b** in **2** was carried out and the results are shown in Table 1.‡



1a-b



2

$$R{-}SH \xrightarrow[\text{[bmim] [BF}_4\text{], RT}]{\text{CoPc, O}_2} RSSR$$

Fig. 1

The disulfides were extracted with ethyl acetate from the ionic liquid after completion of the reaction leaving behind the catalyst solubilized in the ionic liquid. Evaporation of the ethyl acetate under reduced pressure gave the disulfide, which was further purified by column chromatography over a silica gel column using hexane as eluent. The formation of products was confirmed by the comparison of physical and spectroscopic data as well as HPLC retention time with those of authentic samples. UV-visible spectral studies of the oxidation of thiophenol with molecular oxygen catalyzed by **1a** in **2** show that the formation of disulfide resulted from the dimerization of $RS^{\cdot}$ radicals which in turn formed from the reaction of Co(I)–O_2 with RS^-.†[10] The recovered blue ionic liquid containing CoPc was reused for further catalytic reactions and found to have comparable activity upto 5–6 recycling experiments with a slight decrease in the yields of the products in each cycles. Similar results were obtained for **1b** but yields of disulfides were higher than that for **1a**. Further, **1b** showed better catalytic activity than **1a** in the oxidation of thiols with molecular oxygen at room temperature.

The yield of diphenyl disulfide in the oxidation of thiophenol with molecular oxygen catalyzed by **1a** in organic solvents such as THF and DMF were 58 and 82%, respectively, as compared to 95% in ionic liquid under similar conditions. Further, longer reaction times were required in these organic solvents (1–3 h) than in ionic liquids for complete conversion of thiols to disulfides and separation of the product from the reaction mixture is tedious.

In summary, efficient biomimetic oxidation of thiols to disulfides with molecular oxygen catalyzed by cobalt(II)

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† Electronic supplementary information (ESI) available: experimental. See http://www.rsc.org/suppdata/cc/b3/b305888c/

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Table 1 Oxidation of thiols to disulfides with molecular oxygen catalyzed by **1a** and **1b** immobilized in ionic liquid **2**[a]

Run	Substrate	Catalyst	Time/min	Yield of disulfide[b](%)	Turnovers[c]	mp or bp/mmHg (Lit. mp or bp)
1	C_6H_5SH	**1a**	45	95 (92)[d,e,f]	2.07 × 10^4	57–59 (59–60)[24]
2	C_6H_5SH	**1b**	45	99 (95)[d]	2.16 × 10^4	
3	4-MeC_6H_4SH	**1a**	35	99 (97)[d]	2.44 × 10^4	51–53 (52–56)[25]
4	2-$H_2NC_6H_4SH$	**1a**	60	95 (89)[d]	2.36 × 10^4	90–92 (91–93)[26]
5	2-Mercaptopurine	**1a**	60	83	2.50 × 10^4	241–244
6	2-Mercaptopyridine	**1a**	60	86 (81)[d]	1.89 × 10^4	56–57 (57–58)[25]
7	$C_6H_5CH_2SH$	**1a**	45	93 (90)[d]	2.29 × 10^4	70–73 (71–72)[25]
8	$C_6H_5CH_2SH$	**1b**	45	97	2.39 × 10^4	
9	$HOCH_2CH_2SH$	**1a**	45	91 (84)[d]	1.40 × 10^4	113/7 (115/7)[24]
10	n-C_4H_9SH	**1a**	45	92 (91)[d]	1.64 × 10^4	223–226 (226)[25]
11	n-C_4H_9SH	**1b**	45	97	1.73 × 10^4	
11	n-$C_8H_{17}SH$	**1a**	60	87 (85)[d]	2.52 × 10^4	185–187/6 (187/6)[24]
12	n-$C_8H_{17}SH$	**1b**	60	93	2.69 × 10^4	

[a] All reactions were carried out using thiol (1.0 mmol), CoPc (1.0 × 10^{-2} mmol) in [bmim][BF_4] (2.0 mL). [b] Yields are based on starting material and are calculated by HPLC analysis (μ-bondapak C_{18} reverse phase column, methanol : water = 60 : 40 v/v, flow rate = 0.5 ml min^{-1}, monitored at 220 nm). [c] Based on yield of disulfide. [d] Isolated yields. [e] 7% of diphenyl disulfide was also obtained in absence of catalyst **1a**. [f] Diphenylsulfide was formed in 58 and 82% yield with 1.26 × 10^4 and 1.79 × 10^4 turnovers in THF and DMF, respectively.

phthalocyanines (**1a** and **1b**) immobilized in imidazolium ionic liquid (**2**) has been achieved. The reactions are clean and work-up of the reaction products is easy. The catalysts (**1a** and **1b**) immobilized in the ionic liquid (**2**) are easily recyclable and can be reused in further reactions without much loss of catalytic activity. The cobalt(II) tetranitrophthalocyanine (**1b**) proved to be a better catalyst than cobalt(II) phthalocyanine (**1a**). Hence, Co(II) phthalocyanine immobilized in ionic liquid can be used for petroleum purification and oxidative treatment of waste water or industrial effluents.

Notes and references

‡ The required ionic liquid [bmim][BF_4] was prepared according to the reported procedure[20] by the alkylation of 1-methylimidazole with 1-bromobutane followed by substitution of bromide anion with tetrafluoroborate in acetone.[27] ^1H NMR ($CDCl_3$, 300 MHz, δ ppm): 8.98 (s, 1H, C–2H), 7.49 (s, 2H, C–4H & C–5H), 4.21 (t, J = 7.11 Hz, 2H, $NCH_2CH_2CH_2CH_3$), 4.01 (s, 3H, NCH_3), 1.85 (p, J = 7.20 Hz, 2H, –$NCH_2CH_2CH_2CH_3$), 1.35 (sexet, J = 7.20 Hz, 2H, $NCH_2CH_2CH_2CH_3$), 0.91 (t, J = 7.12 Hz, 3H, $NCH_2CH_2CH_2CH_3$). ^{13}C NMR ($CDCl_3$, 75 MHz, δ ppm): 13.27, 19.23, 31.87, 36.13, 49.57, 122.49, 123.79 and 136.12.

Typical procedure for oxidation of thiols with molecular oxygen catalyzed by CoPc or CoTNPc immobilized in ionic liquid [bmim][BF_4]: The solid CoPc or CoTNPc (0.01 mmol) was immobilized in [bmim][BF_4] (2 mL) by stirring and thiol (1.0 mmol) was added to the above mixture in a round bottomed flask. Oxygen gas was bubbled through the reaction mixture while stirring for 45–60 min at room temp. Progress of the reaction was monitored by HPLC. The ionic liquid layer was extracted with ethyl acetate (3 × 10 mL). The combined extracts were concentrated under reduced pressure and the residue was purified by column chromatography. The [bmim][BF_4] containing CoPc or CoTNPc was recovered and reused for the next oxidation.

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