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Highly selective and efficient oxidation of sulfide to sulfoxide catalyzed by platinum porphyrins

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ABSTRACT: Two platinum porphyrins, *meso*-tetramesitylporphyrinatoplatinum and *meso*-tetrakis(pentaflourophenyl) porphyrinatoplatinum, are explored for catalytic application in the selective oxidation of sulfide to sulfoxide by iodosylbenzene. The obtained overall turnover number of 90,000 in the oxidation of thioanisole in the presence of *meso*-tetrakis(pentaflourophenyl) porphyrinatoplatinum indicates the pronounced catalytic activity of the platinum porphyrins. Perfect selectivity toward sulfoxide or sulfone also was achieved *via* stoichiometric control of reactants.

KEYWORDS: sulfides, selective oxidation, platinum porphyrins, high turnover number.

INTRODUCTION

Oxidation of sulfides is very important from both synthetic and mechanistic investigation points of view. Sulfoxides are valuable compounds owning to their pharmaceutical, industrial and synthetic applications [1–3]. Oxidation of sulfides to sulfoxides as the main route to get sulfoxides has been the subject of extensive studies [4–11]. Over-oxidation of sulfides to sulfones is the major problem of the oxidation. Therefore, selective oxidation of sulfides to sulfoxides under mild and green conditions has remained a challenge thus far [12–20]. On the other hand, since sulfide and sulfoxide have different nucleophilic tendency, some groups use sulfide oxidation to get some clue about the active oxidizing species of a catalytic system [21, 22].

Metalloporphyrins particularly manganese and iron porphyrins have been investigated extensively as models of CPY-450 enzymes to oxidize organic substrates including sulfides [23–29]. While a high-valent metal oxo species is responsible for oxidation of substrate in the presence of metal porphyrins and related macrocycles [24, 30–33] but there are some reports that confirm the existence of a six-coordinated peroxo-type species as an oxidant which is less reactive than a metal oxo species and therefore can control the reactivity and selectivity of the catalyst [34–36].

Recently, the formation of Pt^{IV}(porp$^{+\bullet}$)(OH)$_2$ species as the active oxidizing species in the catalytic oxidation of alkenes by platinum porphyrins has been reported by us [37]. Electrochemical formation of this species has also been reported and well-documented by Kadish and co-workers [38, 39]. As a part of our ongoing interest on catalytic activity of platinum porphyrins in oxidation reactions, we examined their catalytic activity in the oxidation of various sulfides.

RESULTS AND DISCUSSION

Catalytic oxidation of thioanisole (as a model substrate) with iodosylbenzene in the presence of *meso*-tetramesitylporphyrinato platinum (PtTMP) has been studied. Blank experiment (Entry 1, Table 1) revealed that the presence of the catalyst is essential for an effective catalytic reaction.

To note, selectivity of the reaction can be controlled by thioanisole to oxidant molar ratio (Entries 2 and 3, Table 1). In the 1:1 molar ratio of the oxidant to thioanisole, sulfoxide is the sole product while in the 3:1 (oxidant/thioanisole) molar ratio, sulfone was exclusively

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◊SPP full member in good standing

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Table 1. Optimization of the molar ratio for {catalyst/thioanisole/PhIO} in catalytic thioanisole oxidation by PtTMP as catalyst[a]

Entry	Molar ratio	Conversion, %[b]	Sulfoxide, %	Sulfones, %	Selectivity to sulfoxide, %
1	0:20:60	—	—	—	—
2	1:20:60	100	—	100	—
3	1:20:20	85	85	—	100
4	1:50:50	90	90	—	100
5	1:60:60	91	91	—	100
6	1:100:100	85(90)[c]	85(90)[c]	—	100(100)[a]
7	1:150:150	70	70	—	100
8	1:200:200	65	65	—	100

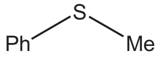
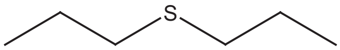
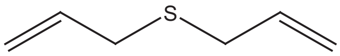
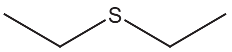
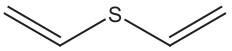
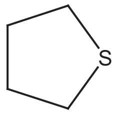
[a] The reactions were all triplicated at room temperature, in CH_2Cl_2 and the average data are reported with ±4% error. GC injections were carried out after 30 min. [b] GC yield is based on starting thioanisole. [c] Numbers in parentheses are for 24 h after starting of the reaction.

Table 2. Sulfoxide yield (%) of thioanisole oxidation in different solvents[a]

Solvent	Time, min		
	30	60	90
CH_2Cl_2	85	88	90
$CHCl_3$	55	70	75
CH_3COCH_3	Trace[b]	50	80
CH_3CN	Trace	Trace	Trace
CH_2ClCH_2Cl	58	80	80 (6.3)[c]

[a] PtTMP and PhIO were used as catalyst and oxidant respectively and the molar ratio for {catalyst/thioanisole/PhIO} is {1/100/100}. [b] The catalyst was dissolved gradually in acetone. [c] 6.3% sulfone was observed.

Table 3. Yield (%) of various sulfides oxidation by two different Pt-porphyrins using PhIO as oxidant[a]

Entry	Sulfide	Catalyst	
		PtTMP	PtTPFPP
1		85	86(14)[b]
2		60	80(12)[b]
3		13	25
4		82	100
5		60	37(18)[b]
6		100	100

[a] The reactions were carried out at room temperature, in CH_2Cl_2. The molar ratio for {catalyst/substrate/PhIO} is {1/100/100}. GC injections were carried out after 30 min. [b] Numbers in parentheses are the yield of sulfone.

achieved. These results confirm that the over-oxidation of sulfoxide depends on the oxidant to sulfide molar ratio. The effect of different catalyst concentrations was also explored and the results are presented in Table 1 (Entries 4–8). The obtained conversion for "1:100:100" molar ratio is just 6% less than that of "1:60:60" molar ratio, while the molar ratio in the former is almost half of the latter. So, the conditions given in Entry 6 were chosen as the optimized conditions.

The influence of different solvents on the oxidation of thioanisole was studied with the results presented in Table 2. The lowest catalytic activity in the acetone and acetonitrile may possibly be due to their low solubility in these solvents because the catalyst was dissolved overtime in acetone and showed catalytic activity.

In order to find the effect of the other oxidants on the oxidation reaction, catalytic oxidation of thioanisole with urea hydrogen peroxide (UHP), hydrogen peroxide (H_2O_2) and *tert*-butyl hydroperoxide (TBHP) has been studied. No oxidation product was achieved in the presence of these oxidants, probably because these oxidants can only oxidize Pt^{II}(porp) to $Pt^{IV}(porp)(OH)_2$ that is inactive in oxidation reactions while oxidants such as iodosylbenzene(PhIO) or *meta*-chloroperbenzoic acid (*m*-CPBA) can oxidize Pt^{II}(porp) by three electrons to $Pt^{IV}(porp^{+\bullet})(OH)_2$ which is a mild oxidant [37].

A variety of sulfides were oxidized by two platinum porphyrins, *meso*-tetrakis(pentaflourophenyl) porphyrinatoplatinum (PtTPFPP) and *meso*-tetramesitylporphyrinatoplatinum (PtTMP) which have very different

Table 4. Oxidation of thioanisole using PhIO catalyzed by some metal porphyrins[a]

Catalyst	Conversion, %	Sulfoxide, %	Sulfone, %	Selectivity to sulfoxide, %
PtTMP	85	85	—	100
Fe(TMP)Cl	53	43	10	80
Mn(TMP)Cl[b]	78	62	16	80

[a] The reactions were carried out at room temperature, in CH_2Cl_2 as solvent. The molar ratio for {catalyst/substrate/PhIO} is {1/100/100} and GC injections were carried out after 30 min. [b] Imidazol used as co-catalyst with 20 fold of Mn(TMP)Cl.

electronic density on the porphyrin ring (Table 3). The results show that both reactivity and selectivity of the catalysts depend on electronic properties of platinum porphyrins. The higher conversion was achieved in the presence of PtTPFPP. This may be due to the electron withdrawing effects of the fluorine atoms which caused higher activity of the $Pt^{IV}(porp^{+\bullet})(OH)_2$ species. Sulfone formation in some cases confirmed the higher activity of PtTPFPP compared to PtTMP [40].

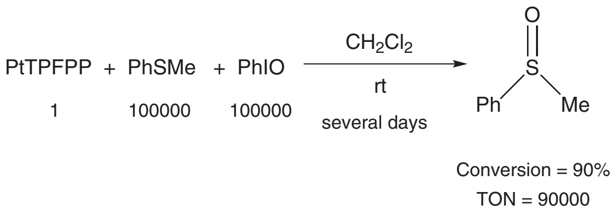
As can be seen from Table 3, the reactivity of the catalysts also depend on electronic and steric properties sulfides although electronic effects are much more impressive (Entries 2 and 3, Table 3). The more electron density on sulfur, the higher conversion.

The catalytic activity of PtTMP has been compared with iron and manganese counterparts (Table 4). Pt-porphyrin shows not only higher activity than Fe- or Mn-porphyrins but also exhibits perfect selectivity for sulfoxide product.

Higher selectivity of the platinum porphyrins is due to the formation of $Pt^{IV}(porp^{+\bullet})(OH)_2$ species [37] which is responsible for oxidation of sulfides while in the case of Fe- or Mn-porphyrins, a high-valent metal oxo species will be formed which is highly reactive [36].

Stability towards oxidative degradation is another salient feature of the platinum porphyrins. Higher activity of platinum porphyrins arises from this outstanding feature of platinum porphyrins compared with iron or manganese porphyrins. Therefore, as anticipated, the catalyst shows almost no degradation after the experiment in contrast to the reports for Mn- or Fe-porphyrins which undergo degradation very quickly [41, 42].

High turnover number is anticipated for this catalytic system due to outstanding stability of the platinum porphyrins towards oxidative degradation. Therefore, thioanisole oxidation catalyzed by PtTPFPP in large-scale was investigated (Scheme 1) and it should be noted that the turnover number (TON) of the catalyst could exceed 90,000, due to its high oxidative stability and negligible degradation (see Fig. 1). As it is obvious from Fig. 1, there is just small demetalation of the PtTPFPP catalyst. To the best of our knowledge, in the oxidation reaction systems for sulfide to sulfoxide catalyzed by metalloporphyrins, such a high TON value has been reported just for ruthenium porphyrins [43].



Scheme 1. Oxidation of thioanisole in large-scale catalyzed by PtTPFPP

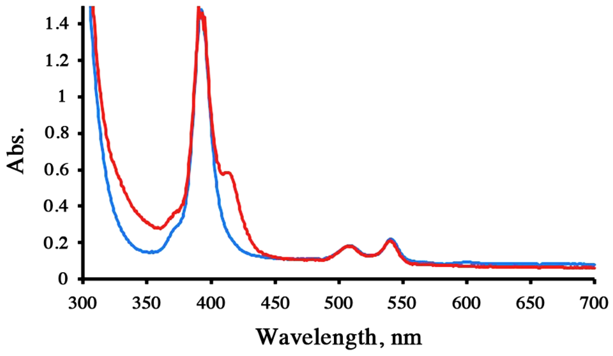


Fig. 1. UV-vis spectra of reaction mixture (a) before starting the reaction (blue) and (b) after 2 days from the reaction (red)

The turnover number is calculated by the following equation:

$$TON = \frac{\text{mmolsulfoxide}}{\text{mmolcatalyst}} \tag{1}$$

EXPERIMENTAL

All chemicals and solvents were purchased from Merck, Fluka or Aldrich chemical companies and used as recieved. The free bases, *meso*-tetraphenylporphyrin (H_2TPP), *meso*-tetramesitylporphyrin (H_2TMP) and *meso*-tetrakis(pentaflourophenyl)porphyrin (H_2TPFPP), were prepared according to the literature [44]. Free base porphyrins were metalated with platinum(II) chloride, $PtCl_2$, as described in the literature to give corresponding *meso*-tetraphenylporphyrinato platinum (PtTPP), *meso*-tetramesitylporphyrinato platinum (PtTMP) and *meso*-tetrakis(penta-flourophenyl)porphyrin (PtTPFPP)

Table 5. Spectroscopic data for prepared porphyrins

Compound	UV-vis		^{1}H NMR
	Soret	Q-bands	
H_2TMP[a]	418	515, 548, 592, 646	
PtTMP	402	510, 540	8.56, 1.85, 7.25, 2.6
H_2TPFPP[a]	412	506, 584, 645	
PtTPFPP	392	508, 539	8.83

[a] ^{1}H NMR spectra for these poprhyrins weren't recorded because they have been well-known.

complexes [45]. Some spectroscopic data for the prepared porphyrins are given in Table 5. Iodosylbenzene was obtained by the hydrolysis of iodosylbenzene diacetates [46].

Stock solutions of the platinum porphyrins (3×10^{-3} M) were prepared in CH_2Cl_2. In a 10 mL round-bottom flask, the reagents were added in the following order: sulfide (0.3 mmol), catalyst (3×10^{-3} mmol), iodosylbenzene, PhIO, (0.3 mmol) was then added to the reaction mixture at room temperature. The mixture was stirred for 30 min and then was analyzed by gas chromatography.

CONCLUSION

In summary, platinum porphyrins oxidize sulfides to sulfoxides or sulfones with 100 percent selectivity using controlled stoichiometry of the reaction. Platinum porphyrin degradation under reaction conditions is negligible, therefore high turnover number in sulfide oxidation was observed. Adjusted catalytic activity of the active oxidant $Pt^{IV}(porp^{+\bullet})(OH)_2$ results in perfect selectivity toward sulfoxide or sulfone via stoichiometric control of reactants.

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