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COBALT PHTHALOCYANINE MEDIATED AEROBIC OXIDATION OF THIOLS: A SIMPLE AND CONVENIENT PREPARATION OF DISULPHIDES

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COBALT PHTHALOCYANINE MEDIATED AEROBIC OXIDATION OF THIOLS: A SIMPLE AND CONVENIENT PREPARATION OF DISULPHIDES

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ABSTRACT

Cobalt phthalocyaninetetrasulphonamide/tetrasodium salt of cobalt tetrasulphophthalocyanine catalyzed oxidation with molecular oxygen form a simple, efficient and environmentally acceptable synthetic tool for the oxidation of thiols to disulphides in excellent yields, under mild conditions and without any side reactions.

Selective oxidative conversion of thiols to disulphides is an important reaction from a synthetic as well as biological viewpoint^{1,2} and many stoichiometric reagents like manganese dioxide,³ dichromates,⁴ chloro-chromates,⁵ halosilane-chromium trioxide,⁶ diethyl azodicarboxylate,⁷

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nickel peroxide,⁸ chromium peroxide,⁹ diaryl telluroxide,¹⁰ tetrabutyl ammonium cerium (IV) nitrate,¹¹ sodium perborate,¹² silver trifluoromethane sulphonate¹³ and permanganate¹⁴ have been reported to be effective oxidants for this transformation.

The increasing environmental concern surrounding the use of toxic and dangerous oxidants has impelled organic chemists to develop catalytic oxidation methodologies using molecular oxygen as primary oxidants.¹⁵ In this context catalytic oxidation of thiols to disulphides by molecular oxygen using basic alumina,¹⁶ intercalated [Mo^{VI} O₂ {O₂ CC(S)} (Ph₂)₂]²⁻ in Zn^{II}-Al^{III}-layered double hydroxide,¹⁷ cobalt chlorate,¹⁸ Fe (III)/NaI¹⁹ as catalysts have been reported.

In continuation of our studies on oxidation using molecular oxygen as a primary oxidant,^{20–23} we earlier reported that iron (III)-ethylenediaminetetraaceticacid (Fe(III)-EDTA) catalyzed oxidation of thiols to disulfides.²⁴ Although this method worked well for the oxidation of different types of thiols, there have been limitations for the oxidation of tertiary and long chain aliphatic thiols (C₈ and above) and long reaction hours were required due to their low ionization constants. Efforts to overcome this problem by conducting the reaction at higher pH(>11) led to the precipitation of iron oxide due to the low stability of Fe(III)-EDTA.²⁵ In search of a better catalytic system we focused our attention towards metal phthalocyanines which are used for catalytic oxidation of thiols present in petroleum fractions under strongly alkaline conditions.²⁶ We report herein for the first time a simple and convenient synthetic method for the oxidation of thiols¹ to disulphides² in near quantitative yields using molecular oxygen as an oxidant and cobalt phthalocyanine tetrasulphonamide [CoPc(SO₂NH₂)4]²⁷ or tetrasodium salt of cobalt tetrasulphophthalocyanine [CoPc(SO₃Na)4]²⁸ as a catalyst (Scheme 1).



A wide variety of thiols consisting of aliphatic, aromatic, heterocyclic, tertiary and long chain aliphatic thiols was selectively oxidized to their corresponding disulphides in near quantitative yields without any evidence for the formation of corresponding sulphonic acid²⁹ (Tables 1 and 2).

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R	Reaction Time (min)	Disulphide Yield ^a (%)
C ₆ H ₅	40	96
$4-H_3C-C_6H_4$	25	95
4-H ₃ COC ₆ H ₄	30	87
$C_6H_5CH_2$	35	97
2-Pyridyl	22	84
n-C ₄ H ₉	23	93
$n-C_5H_{11}$	25	86
tert-C ₅ H ₁₁	140	84
$n-C_7H_{15}$	28	88
$n-C_8H_{17}$	30	83
$n-C_9H_{19}$	35	88
$n-C_{10}H_{21}$	35	85
$n-C_{12}H_{25}$	40	92
$tert$ - $C_{12}H_{25}$	230	80
<i>n</i> -C ₁₄ H ₂₉	50	95
<i>n</i> -C ₁₆ H ₃₃	70	96
<i>n</i> -C ₁₈ H ₃₇	100	97
$n-C_{19}H_{39}$	120	98
	$\begin{array}{c} R\\ C_{6}H_{5}\\ 4-H_{3}C-C_{6}H_{4}\\ 4-H_{3}COC_{6}H_{4}\\ C_{6}H_{5}CH_{2}\\ 2-Pyridyl\\ n-C_{4}H_{9}\\ n-C_{5}H_{11}\\ tert-C_{5}H_{11}\\ n-C_{7}H_{15}\\ n-C_{8}H_{17}\\ n-C_{9}H_{19}\\ n-C_{10}H_{21}\\ n-C_{12}H_{25}\\ tert-C_{12}H_{25}\\ tert-C_{12}H_{25}\\ n-C_{14}H_{29}\\ n-C_{16}H_{33}\\ n-C_{18}H_{37}\\ n-C_{19}H_{39}\\ \end{array}$	$\begin{tabular}{ c c c } \hline Reaction Time \\ \hline R & (min) \\ \hline \hline C_6H_5 & 40 \\ \hline 4-H_3C-C_6H_4 & 25 \\ \hline 4-H_3COC_6H_4 & 30 \\ \hline C_6H_5CH_2 & 35 \\ \hline 2-Pyridyl & 22 \\ n-C_4H_9 & 23 \\ n-C_5H_{11} & 25 \\ tert-C_5H_{11} & 140 \\ n-C_7H_{15} & 28 \\ n-C_8H_{17} & 30 \\ n-C_9H_{19} & 35 \\ n-C_{12}H_{25} & 40 \\ tert-C_{12}H_{25} & 230 \\ n-C_{14}H_{29} & 50 \\ n-C_{16}H_{33} & 70 \\ n-C_{18}H_{37} & 100 \\ n-C_{19}H_{39} & 120 \\ \hline \end{tabular}$

Table 1. Cobalt Phthalocyaninetetrasulphonamide Catalyzed Oxidation of Thiols (1) to Disulphides (2) with Molecular Oxygen

^aIsolated yield.

Table 2. Tetrasodium Salt of Cobalt Tetrasulphophthalocyanine Catalyzed Oxidation of Thiols (1) to Disulphides (2) with Molecular Oxygen

Entry	R	Reaction Time (min)	Disulphide Yield ^a (%)
1	$4-H_3C-C_6H_4$	30	96
2	4-H ₃ COC ₆ H ₄	32	85
3	tert-C ₅ H ₁₁	150	86
4	$n-C_9H_{19}$	34	85
5	$n-C_{14}H_{29}$	55	90
6	<i>n</i> -C ₁₈ H ₃₇	95	95
7	$n-C_{19}H_{39}$	126	97

^aIsolated yield.

The protocol developed consists of simply bubbling molecular oxygen into a solution of thiols in 1 N NaOH containing cobalt phthalocyaninetetrasulphonamide or tetrasodium salt of cobalt tetra-sulphophthalocyanine catalyst (0.2 mol % of the thiol) under ambient conditions, until the completion of the reaction (indicated by change of reaction mixture colour from black to blue). Tertiary thiols were found to be less reactive and require longer reaction time. In the case of aliphatic thiols the reactivity decreases with the increase in chain length and accordingly the thiols with longer chain length require more reaction time.

Results presented in Tables 1 and 2 show that both cobalt phthalocyaninetetrasulphonamide and tetrasodium salt of cobalt tetrasulphophthalocyanine exhibit comparable catalytic activities in the oxidation of different types of thiols. It appears that catalytic activity relates to the cobalt phthalocyanine, and the groups attached (SO₂NH₂, SO₃Na) are essentially required for solubilizing the cobalt phthalocyanine in aqueous medium.

To evaluate the catalytic effects of cobalt phthalocyaninetetrasulphonamide and tetrasodium salt of cobalt tetrasulphophthalocyanine, experiments were carried out under similar conditions but without catalysts. The results showed that there was no oxidation of 1-octanethiol to corresponding disulphide even after 24 h.

With a view to determine the effect of pH, we studied the cobalt phthalocyaninetetrasulphonamide catalyzed oxidation of thiophenol at different pH. These results are presented in Table 3 and clearly show that this reaction was highly dependent upon pH of the system and required less reaction times at higher pH. To determine the effect of catalyst concentration in these reactions, experiments were carried out with thiophenol using different quantities of cobalt phthalocyaninetetrasulphonamide catalyst. These results in Table 4 show that the catalyst concentration does not have a significant effect on the reaction time.

Entry	R	pH	Reaction Time (min)
1	C ₆ H ₅	7.00	145
2	C_6H_5	8.50	65
3	C_6H_5	11.0	50
4	C_6H_5	14.00	40

Table 3. Effect of pH in Cobalt Pthalocyaninetetrasulphonamide Catalyzed Oxidation of Thiophenol to Diphenyl Disulphide with Molecular Oxygen

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Table 4. Effect of Catalyst Concentration in Cobalt Pthalocyaninetetrasulphonamide Catalyzed Oxidation of Thiophenol to Diphenyl Disulphide with Molecular Oxygen

Entry	R	Catalyst Concentration (mol %)	Reaction Time (min)
1	C_6H_5	0.2	40
2	C ₆ H ₅	0.5	35
3	C_6H_5	2.0	27
4	C_6H_5	5.0	17

In conclusion, simplicity of the system, excellent yields, wide applicability and reasonable reaction times make cobalt phthalocyaninetetrasulphonamide/tetrasodium salt of cobalt tetrasulphophthalocyanine catalyzed oxidation with molecular oxygen an attractive and environmentally acceptable synthetic tool for the oxidation of thiols to disulphides.

EXPERIMENTAL

Cobalt phthalocyaninetetrasulphonamide was prepared following the literature procedure reported by Agrawal et al.²⁷ and its structure was established by FAB mass spectral and elemental analysis. Tetrasodium salt of cobalt tetrasulphophthalocyanine dihydrate was prepared from 4-sulphophthalic acid essentially employing the procedure reported by Weber and Busch.²⁸

A typical procedure for the oxidation of thiol to disulphide is as follows: molecular oxygen was bubbled into the stirred solution of 1-octanethiol (7.32 g, 50 mmol) and cobalt phthalocyanine-tetrasulphonamide (0.088 g, 0.1 mmol) in 1 N NaOH (250 ml, water), contained in a 500 ml two-necked round-bottomed flask fitted with a gas inlet tube and a condenser for 5 min. The completion of the reaction was indicated by the change of reaction mixture colour from black to blue. The reaction mixture was stirred further for an additional 5 min, and then extracted with dichlor-omethane (2×100 ml), organically phase dried over anhydrous sodium sulphate. Evaporation of the solvent and distillation at the reduced pressure ($185-187^{\circ}$ C at 6 torr) yielded dioctyl disulphide (6.04 g, 83%) as oily liquid. Similarly, disulphides from aliphatic thiols (Entries 6–14, Table 1) were prepared. The disulphides from aromatic heterocyclic thiols (Entries 1–5, Table 1) and aliphatic thiols (Entries 15–18, Table 1) were prepared by conducting the reactions using 10 mmol of thiol similarly, and evaporation of the dichloromethane followed by recrystallization yielded pure disulphides. The products were identified by comparing their physical spectral data and GC retention times with those of authentic samples.

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