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Selective and mild oxidation of thiols to sulfonic acids by hydrogen peroxide catalyzed by methyltrioxorhenium

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Abstract

Aromatic and aliphatic thiols are oxidized in acetonitrile at 20 °C by hydrogen peroxide in the presence of methyltrioxorhenium as the catalyst to yield the corresponding sulfonic acids in high isolated yields (85–94%).

Keywords: Oxidation; Thiol; Hydrogen peroxide; Sulfonic acid; Methyltrioxorhenium

Sulfonic acids and their derivatives represent an important class of compounds used industrially for various applications as surfactants, dyes, animal feeds, pesticides, and pharmaceuticals. Many aliphatic sulfonic acid derivatives display a wide range of pharmacological activity as well as numerous aromatic sulfonic acids are active medicinal agents, useful in treatment of a variety of infections.[1]

The synthetic protocols mostly used in the literature for their preparation are based both on the oxidation of different types of sulfur-containing functional groups[2] and on the direct sulfonation[2,3] of aromatic compounds.[4]

The oxidation of thiols by many oxidizing agents[2,5] is one of the classical methods for the preparation of aliphatic and aromatic sulfonic acids.

Some of these methods suffer from some disadvantages such as long reaction times, difficult workup, low yields, requirement of strong oxidizing agents, strong acidic or basic media, and in some cases use of expensive, dangerous, and harmful to environment reagents.

Recently, techniques for the preparation of mesoporous silica functionalized with sulfonic acid groups have employed a thiol strategy involving grafting or sol–gel route, followed by hydrogen peroxide oxidation of thiol group under strong acidic conditions.[6]

Among eco-compatible oxidants, hydrogen peroxide represents the ideal candidate, because it has a high active oxygen content, it is environmentally friendly, readily available, and produces only water as a by-product.[7]

In the last decade, methyltrioxorhenium CH_3ReO_3 (MTO) in association with hydrogen peroxide has stood out as an appealing oxidant catalytic system, thanks to its high efficiency and selectivity shown in many types of synthetic transformations.

In fact the MTO/H_2O_2 system, under rather mild conditions, is able to oxidize a large variety of compounds such as sulfoxides,[8] alkenes,[9] arenes,[10] amines,[11] alcohols,[12] and natural products.[13]

It has been suggested that both a monoperoxo complex $[(CH_3)Re(O)_2(O_2)]$ (**I**) and a diperoxo complex $[(CH_3)ReO(O_2)_2]$ (**II**) are the active oxidant species involved in the oxygen transfer but it is generally accepted that, under oxidation conditions where a large excess of H_2O_2 over MTO (a 100-fold excess) is used, only the diperoxo complex (**II**) species is present in solution.[14]

This Letter reports a mild and convenient one-pot procedure[15] to oxidize, under homogeneous conditions, both aromatic and aliphatic thiols to the corresponding sulfonic acid derivatives in high yields by the MTO/H_2O_2 system at 20 °C (Scheme 1).

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$$\text{R-SH} + 3\text{H}_2\text{O}_2 \xrightarrow[\text{CH}_3\text{CN, 20 °C}]{\text{MTO}} \text{R-SO}_3\text{H} + 3\text{H}_2\text{O}$$

Scheme 1. Oxidation of aromatic and aliphatic thiols to sulfonic acids.

Table 1

Oxidation of thiols with CH_3ReO_3/H_2O_2 in CH_3CN at 20 °C[a]

Entry	Substrate	Product	Isolated yields (%)
1	C_6H_5SH	$C_6H_5SO_3H$	85
2	$4\text{-}CH_3\text{-}C_6H_5SH$	$4\text{-}CH_3\text{-}C_6H_5SO_3H$	87
3	$4\text{-}OCH_3\text{-}C_6H_5SH$	$4\text{-}OCH_3\text{-}C_6H_5SO_3H$	91
4	$4\text{-}NO_2\text{-}C_6H_5SH$	$4\text{-}NO_2\text{-}C_6H_5SO_3H$	92[b]
5	$4\text{-}Cl\text{-}C_6H_5SH$	$4\text{-}Cl\text{-}C_6H_5SO_3H$	85
6	$C_6H_5CH_2SH$	$C_6H_5CH_2SO_3H$	93
7	2-Naph-SH	$2\text{-Naph-}SO_3H$	94
8	$CH_3(CH_2)_{10}CH_2SH$	$CH_3(CH_2)_{10}CH_2SO_3H$	90[b]
9	$CH_3(CH_2)_{16}CH_2SH$	$CH_3(CH_2)_{16}CH_2SO_3H$	91[c]
10	C_6H_5SH	$C_6H_5SO_3H$	88[d]

[a] General reaction conditions: thiol (1.2 mmol), H_2O_2 (30%, 12 mmol), MTO (0.12 mmol), CH_3CN (10 mL), 20 °C ($t = 1/4$–2 h), conversion 100%.

[b] In $CHCl_3/CH_3CN$ (20/80).

[c] In THF.

[d] Reaction conditions: thiol (1.2 mmol), H_2O_2(30%, 12 mmol), MTO (0.012 mmol), CH_3CN (10 mL), 20 °C ($t = 1/2$ h), conversion 100%.

The data reported in Table 1 are the first examples of the direct transformations of thiols to sulfonic acids catalyzed by MTO. It is interesting to note that the reaction works as well with short reaction times and in good yields employing 1% of catalyst instead of 10% (entries 1 and 10).

Other metals than rhenium lead to the formation of the corresponding disulfides.[2] As a matter of fact, molybdenum oxo diperoxo complex $MoO(O_2)_2HMPA$ oxidizes $C_6H_5CH_2SH$ exclusively to the corresponding disulfide in CH_3CN at 25 °C,[2c] according to the lower reactivity of Mo(VI) diperoxo complex compared with that of the corresponding rhenium diperoxo derivative.

Moreover, electron-donating or withdrawing groups on the aromatic ring do not affect the efficiency of the reaction (entries 1–5).

The two oxidation steps leading to sulfonic acids from thiols can start from a proton-coupled electron transfer leading to disulfides (a) or from an S-oxygen transfer step (b), respectively:[2b]

$$RSH \rightarrow RS^{\cdot} \rightarrow RSSR \rightarrow\rightarrow\rightarrow RSO_3H \tag{a}$$

$$RSH \rightarrow (RSOH) \rightarrow RSO_2H \rightarrow RSO_3H \tag{b}$$

We are not able at this stage to suggest a mechanism for the oxidation reaction of thiols to sulfonic acids by H_2O_2/MTO, even if the not detected intermediate disulfides in the oxidation step might indicate the pathway (b) as more probable.

In conclusion, the oxidant system MTO/H_2O_2 provides a new entry for the synthesis of sulfonic acids from thiols in high yields by an efficient, simple, environmentally friendly, and mild protocol.

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15. The following general oxidation procedure was applied to all thiols reported in Table 1. To a solution of 30% hydrogen peroxide (12 mmol, 10 equiv) in CH_3CN (3 mL) at 20 °C was added a solution of methyltrioxorhenium (Aldrich) (0.12 mmol, 0.1 equiv) in CH_3CN (2 mL). This yellow mixture was stirred for 1 min. Then a solution of thiol (1.2 mmol, 1 equiv) in CH_3CN (5 mL) was added and the stirring was continued for a suitable reaction time. After completing the reaction (monitored by TLC), a catalytic amount of MnO_2 was added.[16] The organic phase was concentrated under reduced pressure to afford the crude product, which was purified by column chromatography (chloroform and acetonitrile as eluents) over silicic

acid (100 mesh, Aldrich) for aromatic thiols and over silica gel (Lichroprep RP-18, 25–40 μm, Merck) for the 1-dodecanesulfonic acid (acetonitrile as eluent). The 1-octadecanesulfonic acid was obtained as a white precipitate after filtration and washing with acetonitrile during the concentration under reduced pressure. All the products are known compounds and were easily identified by comparison of their spectroscopic data with those reported.[3,4,17]

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