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Selective oxidation reactions of diaryl- and dialkyldisulfides to sulfonic acids by CH_3ReO_3/hydrogen peroxide

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ABSTRACT

Diaryl- and dialkyl disulfides were oxidized in acetonitrile at 20 °C by CH_3ReO_3/H_2O_2 oxidant system to yield selectively the corresponding sulfonic acids in short reaction times and in high yields.

Sulfonic acids and their derivatives are very useful chemicals which industrially find many applications. For instance, free acids are widely used as catalysts in organic synthesis[1] while their salts and other derivatives form the basis for the manufacture of detergents, water-soluble dyes, and catalysts, sulfonamide pharmaceuticals and ion-exchange resins.[2]

Several methods are available for the synthesis of sulfonic acids. Aromatic sulfonic acids are obtained generally by direct sulfonation of aromatic compounds,[3,4] whereas oxidation of sulfur-containing functional group compounds and reactions of organometallic compounds with amine complexes of sulfur trioxide[4] represent some protocols used to prepare aliphatic sulfonic acids.

Sulfonic acids have classically been prepared by the oxidation of thiols by several oxidizing agents.[5,6] Some of these procedures suffer from a variety of disadvantages as long reaction times and indirect and multi-step routes. However, the oxidation routes of organic sulfur compounds involving peroxides and particularly hydrogen peroxide are preferred because they are often more convenient, very selective, and environmentally friendly.[7]

Recently, we have reported a mild and convenient one-pot procedure to oxidize various aromatic and aliphatic thiols, under homogeneous conditions, to the corresponding sulfonic acids in high yields employing as a catalyst CH_3ReO_3 (MTO) in association with H_2O_2.[8,9]

The MTO/H_2O_2 system, which generates in situ two electrophilic oxidant species, a monoperoxo complex $[(CH_3)Re(O)_2(O_2)]$ and a diperoxo complex $[(CH_3)ReO(O_2)_2]$, requires a work-up protocol that is quite simple and produces water as the only byproduct.[10,11]

For the formation of sulfonic acids by thiol oxidation a reaction pathway[5,7] has been suggested starting from a proton-coupled electron transfer step leading to disulfides (a) or from an *S*-oxygen transfer step (b) (Scheme 1).

The possibility that disulfides might be intermediates in the oxidation reactions of thiols (route a) by MTO/H_2O_2 is of interest both from a mechanistic and a synthetic point of view, since the larger availability of disulfides than thiols.

Therefore we deemed worthwhile to start a study on the oxidation reactions of aromatic and aliphatic disulfides by the MTO/H_2O_2 system in CH_3CN at 20 °C, under homogeneous conditions[12] (Scheme 2).

$$\mathrm{RSH} \longrightarrow \mathrm{RSSR} \longrightarrow \longrightarrow \longrightarrow \mathrm{RSO_3H} \qquad \text{(a)}$$

$$\mathrm{RSH} \longrightarrow \mathrm{(RSOH)} \longrightarrow \mathrm{RSO_2H} \longrightarrow \mathrm{RSO_3H} \quad \text{(b)}$$

Scheme 1. Suggested reaction pathways for the formation of sulfonic acids by thiol oxidation.

$$\mathrm{R{-}SS{-}R} + 5\,\mathrm{H_2O_2} \xrightarrow[\mathrm{CH_3CN,\ 20^\circ C}]{\mathrm{MTO}} 2\,\mathrm{RSO_3H} + 4\,\mathrm{H_2O}$$

Scheme 2. Oxidation of aromatic and aliphatic disulfides to sulfonic acids.

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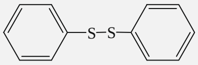
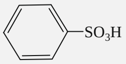
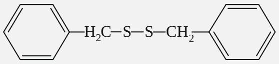
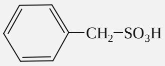
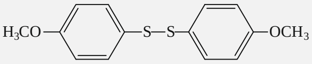
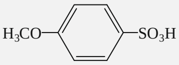
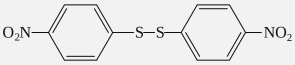
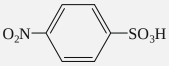
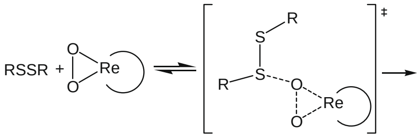
Table 1
Oxidation reactions of disulfides to sulfonic acids with CH_3ReO_3/H_2O_2 in CH_3CN at 20°C[a]

Entry	Substrate[b]	Time (min)	Product	Isolated yields (%)
1		25		98
2		20		81
3		10		98
4		>60		96[c]
5	$CH_3CH_2S–SCH_2CH_3$	<1	$CH_3CH_2SO_3H$	80
6	$CH_3CH_2CH_2S–SCH_2CH_2CH_3$	<1	$CH_3CH_2CH_2SO_3H$	90
7	$(CH_3)_2CHS–SCH(CH_3)_2$	<1	$(CH_3)_2CHSO_3H$	85
8	$CH_3(CH_2)_2CH_2S–SCH_2(CH_2)_2CH_3$	<1	$CH_3(CH_2)_2CH_2SO_3H$	87

[a] Reaction conditions: disulfide (0.6 mmol), 35% H_2O_2 (6.0 mmol), MTO (0.006 mmol) in CH_3CN (5 mL). Excess of H_2O_2 is removed by catalytic amounts of MnO_2.
[b] Conversion 100%.
[c] In CH_2Cl_2/CH_3CN (80/20; 9 mL).



Scheme 3. Nucleophilic attack of disulfide onto a peroxide oxygen of the rhenium peroxo complex generated in situ.

Pertinent results, reported in Table 1, reveal that disulfides are oxidized selectively to the corresponding sulfonic acids by the MTO/H_2O_2 system in high yields. It is interesting to observe that the reaction works well employing 1% of catalyst. Dialkyl disulfides react much faster than diaryl disulfides completing the reaction in less than 1 min. Electron-donating substituents (entry 3) in the aromatic nucleus reduce reaction time whereas electron-withdrawing groups (entry 4) slow down the reaction rate, but the reaction is still efficient. Note that to the best of our knowledge, direct oxidation of organic disulfides containing nitro groups to the corresponding sulfonic acids is unprecedented. These findings seem in accord with an electrophilic oxygen transfer[13] step which envisages a rate-determining nucleophilic attack of disulfide onto a peroxide oxygen of the rhenium peroxo complex generated in situ (Scheme 3).

The results displayed in Table 1 compared with those reported previously[9] for the oxidation reactions of thiols by the MTO/H_2O_2 oxidant system seem consistent with the intermediacy of disulfides in the oxidation of thiols to sulfonic acids. In fact, under the same experimental conditions adopted for the oxidation reactions of thiols by MTO/H_2O_2, disulfides structurally correlated to thiols yield the same sulfonic acids with reaction times shorter than thiols themselves.

In conclusion this one-pot procedure to obtain aromatic and aliphatic sulfonic acids from disulfides is very simple and very selective, requires short reaction times, and affords high yields. The use of hydrogen peroxide as the oxygen donor and the larger availability of disulfides than thiols make very appealing this environmentally friendly method.

Acknowledgments

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