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Solvent-free chemoselective oxidation of thioethers and thiophenes by mechanical milling

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Organosulphur compounds can be easily and selectively oxidized to sulfones using a small excess of Oxones (1.6 eq.) under solventless mechanical milling conditions. This green procedure has been efficiently applied to a series of model compounds and to the desulphurization of medium/high sulphur content paraffins (up to 3000 mg kg^{-1}).

Petroleum and paraffin contain a large variety of sulphur compounds (thiols, sulfides, disulfides, thiophenes, benzo and dibenzothiophenes) which generate SO_2 and airborne particulate emissions during combustion. Catalytic hydro-desulphurization (HDS) has been the accepted method for the removal of organosulphur compounds for some time. In this process H_2 is converted to H_2S and subsequently reacted with O_2 in the Claus process to provide H_2O and elemental sulphur. Various factors affect HDS catalyst performance and these include the type of feed material and the chemical nature of the organosulphur compounds (i.e. aliphatic sulphur is more easily removed than aromatic sulphur).[1] HDS reactivity follows this order: thiophenes > benzothiophenes > dibenzothiophenes > dimethyldibenzothiophenes.[2] Oxidative desulphurization (ODS) is an interesting alternative, or possibly complementary, process which works by means of a wide range of suitable oxidizing agents, such as peroxy organic acids, hydroperoxides, nitrogen oxides, peroxy salts, ozone, etc.[3] ODS is attracting significant research interest, mainly as a means of treating light oils, because of its ease of use and high efficiency.[4] When using the ODS technique it was found that sulphur compound reactivity was somehow the opposite to what would have been expected from the use of HDS. Generally speaking, the process consists of two steps: (1) oxidation whereby organosulphur compounds are converted into sulfoxides and sulfones, and (2) their subsequent removal by extraction or adsorption. All of these oxidation reactions occur in the heterogeneous phase as either liquid–solid   or liquid–liquid reactions and therefore the optimization of mass and heat transfer is a crucial feature.

While liquid fuels can easily be subjected to power ultrasound[5] or hydrodynamic cavitation,[6] paraffin can only be treated with specific high-shear mixers.[7] We believe that mechanical milling can also be used to treat paraffins that rapidly melt under intense friction. To the best of our knowledge, this is the first study to carry out paraffin ODS and, thanks to the starting material's solid nature (mp 50–80°C), the first process to be carried out under solventless and mechanochemical conditions.
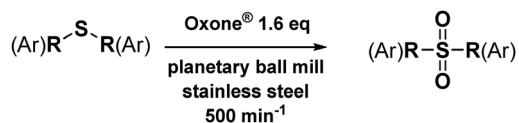
Chemical reactions in ball mills have also attracted large amounts of attention from organic chemists over the last decade.[8,9]

This method allows reactions to be carried out in the solid state and can also reduce solvent use (when required),[10–13] which makes it an attractive option for other application fields as well.[14]

After a preliminary screening of several solid oxidants (sodium persulphate, potassium superoxide, sodium tungstate) we selected Oxones ($2 KHSO_5$, $KHSO_4$, K_2SO_4) for use in our studies. It is a commercially available, white, granular, solid peroxygen that enables green, efficient non-chlorine oxidation and whose reaction by-products are generally recognized as safe. Owing to its high stability and efficiency, Oxones has found many applications[15] in the oxidation of amines,[16] alcohols,[17] aldehydes[18] and ketones,[19] the epoxidation reactions of alkenes,[20] C–H bond oxidation processes[21] and the Baeyer–Villiger reaction.[22] In particular, Oxones can also be applied to sulfoxidation reactions in aqueous acetone or methanol,[23] and to the mechanochemical oxidation of para-substituted anilines to nitrosobenzenes.[24] Yu *et al.* have reported the use of Oxones in the selective oxidation of organic sulfides under stirring (12 h) at 60°C.[25] The sulfoxide/ sulfone ratio was strongly dependent on the solvent (ethanol *vs.* water).

In this communication we report the solventless selective oxidation of several organosulphur compounds to sulfones, under mechanical milling conditions using Oxones, and application of this optimized procedure to the desulphurization of medium to high sulphur content paraffins (Scheme 1).
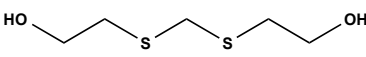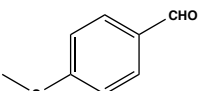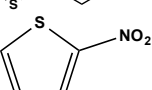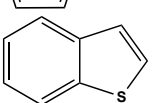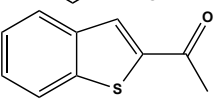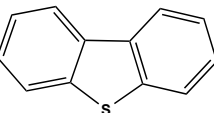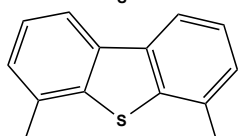
A number of exploratory experiments used 3,6-dithiaoctane- 1,8-diol (Lindlar catalyst poison) and 4-(methylthio)benzaldehyde as model compounds as well as a series of S-heterocycles (thiophene, benzothiophene, dibenzothiophene and substi- tuted derivatives).

$$(Ar)R \overset{S}{\diagdown} R(Ar) \xrightarrow[\substack{\text{planetary ball mill} \\ \text{stainless steel} \\ \text{500 min}^{-1}}]{\text{Oxone}^{®}\text{ 1.6 eq}} (Ar)R - \overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}} - R(Ar)$$

Scheme 1 Chemoselective oxidation of sulphides to sulfones.[26]

All substrates exclusively afforded the sulfone as the oxidation product and no traces of sulfoxides were detected, a fact which effectively highlights the chemoselectivity of mechanochemical oxidation with Oxones. All substrates, apart from nitrothiophene, gave excellent conversions and yields. All the reactions were carried out in low oxidant excess (1 : 1.6 molar ratio) and samples were analyzed by GC-MS[27] after 30 and 90 minutes (Table 1). FTIR, ^{1}H- and ^{13}C-NMR spectra of the isolated products confirmed the sulfone structures.[28] For the sake of comparison with conventional techniques, all the reaction mixtures were simply heated at 80°C for 90 min (neat or in toluene solution under stirring). In all cases only the starting material was detected.

Table 1 Sulphur compound oxidation under mechanical milling conditions[26]

Entry	Substrate	Time (min)	Sulfone	
			Conversion (%)	Yield (%)[a]
1	HO—S—S—OH	30	9	8
		90	100	99
2	CHO, S	30	13	11
		90	100	97
3	S, NO$_2$	30	0	-[b]
		90	0	-[b]
4	benzothiophene	30	35	34
		90	100	98
5	acetyl benzothiophene	30	31	27
		90	100	97
6	dibenzothiophene	30	20	19
		90	100	99
7	dimethyl dibenzothiophene	30	27	25
		90	100	99

a Isolated yields (flash chromatography, PE–EtOAc, 9 : 1 as an eluent).
b Starting material.

The oxidant and its reuse were also investigated in successive reactions with DBT, as it is one of the most common sulphur compounds in petroleum derivatives (initial molar ratio DBT/Oxones 1 : 2). At the end of the reaction, the solid mixture was washed with CHCl$_3$ to recover the organic compounds and to clean the Oxones. This procedure was repeated over three cycles highlighting the fact that Oxones can be easily reused when it is in stoichiometric excess (Table 2).

Table 2. Oxones reuse starting from an 1 : 2 molar excess

Entry	Substrate	Cycles	Yield[a] (%)
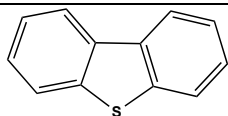
8		1	100
		2	100
		3	< 1

^{a} Isolated yields (flash chromatography, PE–EtOAc, 9 : 1 as an eluent).

With these results at hand, a means to apply this procedure to paraffin ODS was conceived as the organosulphur derivatives tested in the previous reaction were quite similar to those present in petroleum paraffin.[29] We tested the protocol on two types of paraffins, P1 and P2, that differ in their sulphur content (330 and 3000 mg kg^{-1} respectively). P1 is white (mp 50–55°C) while P2 is yellowish (mp 75–80°C).

After oxidative treatment in the ball mill, the paraffins were directly filtered on a thermostatted silica cartridge to remove the sulfones which were easily separated because of their higher polarity. The residual sulphur content after the process was 13 mg kg^{-1} for P1 and 155 mg kg^{-1} for P2.[30]

Differently to what appears at a first glance the method is potentially scalable and suitable large scale ball mills are already used for industrial applications (i.e. cement works factories). The possibility to reuse Oxones when in stoichiometric excess is another important feature for the scaling up of the process. Moreover the use of thermostatted silica cartridges (over the paraffin melting point) enables the filtration without the use of solvents. In pilot plants the full recovery of paraffins from columns or cartridges can be enhanced by means of a stream of hot steam. Although the regulation threshold value of 20 ppm is reached only for one type of paraffin (from 330 ppm to 13 ppm), the cutting down of sulphur content from 3000 to 150 ppm is of high significance, because this product would require a very mild step of catalytic hydrodesulphurization.

In summary a new chemoselective protocol for the oxidation of organosulphur compounds to sulfones has been developed. The solventless mechanochemical reaction with Oxones is effective for the most common organosulphur compounds that are present in paraffin as pollutants and are stubborn to HDS treatment. This makes this ODS procedure an excellent cost-effective compliment to HDS. It is worth noting that the same reaction carried out under stirring at 80°C failed. The low residual sulphur content in the two paraffins tested confirms the potential for application that oxidative desulphurization by mechanical milling presents.

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26 The organosulphur compound (1 mmol) and the Oxones (1.6 mmol) were poured into the milling beaker. We used a planetary ball mill PM100 Retsch GmbH, equipped with a single milling beaker (stainless steel, 125 mL). The solid reaction mixture was milled at 500 min[1] with 25 milling balls (+ = 10 mm, stainless steel). At the half time of reactions, the direction of rotation was inverted. Samples are extracted three times with $CHCl_3$ and the filtered solution is analysed by GC-MS.

27 Gas chromatography-mass spectrometry (GC-MS) analyses were performed in a gas chromatograph Agilent 6890 (Agilent Technologies - USA) fitted with a mass detector Agilent Network 5973, using a 30 m long capillary column, an id of 0.25 mm and a film thickness 0.25 mm. GC conditions were: injection split 1 : 20, injector temperature 250°C, detector temperature 280°C. Gas carrier: helium (1.2 mL min 1), temperature program: from 70°C (2min) to 300°C at 51°C min[1].

28 See ESIz.

29 The paraffin (0.5–1 g) and the Oxones were added to the milling beaker (molar ratio S vs oxidant 1 : 25) and milled as described in ref. 26 for 40 min. The final temperature of the reaction mixture was about 74–76°C. The sample was kept hot (80–90°C) and was directly filtered using a thermostatted silica cartridge (3 g).

30 The total sulphur amount was measured with an elemental analyzer: Multi EAs 5000.