Oxidation of dibenzothiophene by hydrogen peroxide or monopersulfate and metal–sulfophthalocyanine catalysts: an easy access to biphenylsultone or 2-(2′-hydroxybiphenyl)sulfonate under mild conditions

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A catalytic system consisting of metal–sulfophthalocyanines (MPcS) and monopersulfate or hydrogen peroxide as oxidants was effective in the dibenzothiophene oxidative desulfurization with various yields and selectivities. Oxidations were conducted at room temperature in acetonitrile–water mixed solvent. The dibenzothiophene oxidation involved the step by step formation of dibenzothiophene dioxide and biphenylsultone (dibenzo-1,2-oxathiine 2,2-dioxide), followed by hydrolysis to 2(2′-hydroxybiphenyl)sulfonate and finally catalytic desulfurization to 2-hydroxybiphenyl (2-phenylphenol) and sulfuric acid; all the intermediate compounds were identified. Moreover, catalytic over-oxidation of 2-hydroxybiphenyl, with ring fission and formation of various oxidation products, among them carbon dioxide, oxalic and benzoic acid, was also observed. Among the various MPcS catalysts examined (M = Fe, Co and Ru), the ruthenium derivative exhibited the best performances with persulfate and iron derivative with hydrogen peroxide; in both cases the slow step of the process consisted in the oxidation of dibenzothiophene dioxide to biphenylsultone.

Introduction

Dibenzothiophene (DBT) and its alkylated analogues are among the most abundant polycyclic aromatic sulfur hydrocarbons (PASH) in crude oils and are usually selected for model studies of desulfurization, both reductive and oxidative.[1] In December 2000, the US EPA issued revised requirements for sulfur in on-road diesel fuel, with phase-in beginning in mid-2006. This directive lowers the specification from 500 ppm to 15 ppm sulfur.[2] On January 30th, 2003, the European Parliament passed a new resolution on diesel and gasoline quality (P5_TA-PROV(2003)0029). In this regulation the "sulfur-free" fuels are defined as having no more than 10 ppm sulfur content. Both "sulfur-free" gasoline and diesel must be available throughout the EU from 2005, and become mandatory in 2009.

Research has particularly focused on innovative routes for desulfurization approaching cleaner technology and compliance with increasingly stringent regulatory laws. In this context the major issue concerning PASH removal is their recalcitrance to hydrodesulfurization, which makes removal by these conventional technologies unreliable. Two main technologies are close to being introduced in the production stream for diesel, down to the conventional hydrodesulfurization (HDS), both exploiting the relatively facile oxidation of DBT. The first is based on the biological oxidation (BDS) of PASHs (by Enchira Biotech. Corp. and EniTecnologie).[3] It exploits the fact that some classes of bioengineered microorganisms (*i.e. Rhodococcus* sp. IGTS8) are able to promote the aerobic transformation of DBT into 2-hydroxybiphenyl (HBP) and sulfurous and/or sulfuric acid. The physiological role of enzyme systems is to obtain sulfur for growth; the sulfur product being incorporated into cellular biomass *via* sulfur assimilation pathways. The oxidation pathway stops at HBP, which is released into the medium; therefore, the desulfurization of fossil fuels does not decrease the carbon content ("fuel value"). However, several engineering concerns are not addressed fully and a large aqueous phase is required. The other known technology is based on the chemical oxidation (ODS) of PASHs (UniPure Corp.). The UniPure process relies on the facile conversion of thiophenic compounds, among them DBT, to the corresponding sulfones, by using an oxidant carried in an aqueous phase along with a dissolved catalyst.[4] The oxidation is done at near atmospheric pressure and mild temperatures, around 100 °C, and consumes a relatively insignificant amount of oxidant. Conversion to sulfones is completely accomplished with reactor residence times of less than five minutes. However, separation of sulfones is somewhat complicated, since they dissolve at least in part in the oil phase, which must therefore be sent through an extraction step. The product diesel oil then contains 5 ppm or less of sulfur.

The scientific challenge is to devise a one-step biomimetic process operating at room temperature in a biphasic system oil/water and using green co-oxidants, such as oxygen or hydrogen peroxide, which may lead to formation of sulfuric acid, without degrading the hydrocarbon part. The catalyst and the oxidant should be water-soluble, to avoid pollution of the organic phase and allow the regeneration of the catalyst, as well as the products of DBT deep oxidation (sulfonic and/or sulfuric acids). Unfortunately, whereas oxidation of

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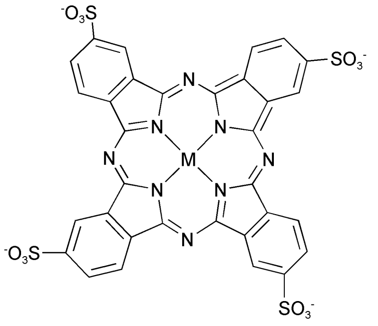

Fig. 1 MPcS.

thioethers, among them DBT, to sulfones is a relatively facile process, sulfones can be further transformed into sulfonic acids only by strong oxidants, such as nitric acid, and oxidative desulfurization is an even rarer event.[5] PASHs are indeed among the most refractory compounds at contaminated sites[6] and the conventional activated sludge process does not effectively degrade these toxic compounds;[7] simple biological systems, such as hemoglobin, horseradish peroxidase and heme–bovine serum albumin, promote the oxidation of DBT to dibenzothiophene monoxide (DBTO) only.[8] A number of effective combinations of catalysts and oxidants have been used to achieve the oxidation of DBT, but most of them however only yield dibenzothiophene dioxide ($DBTO_2$).[9–11] Deep oxidations of DBT are reported to occur upon sonication, yielding desulfurized products, such as hydroxy- and dihydroxy-dibenzothiophenes,[12] or upon exposure to sunlight, to give acidic photoproducts, such as 2-sulfobenzoic acid.[13]

We present here a series of metal–sulfophthalocyanines (Fig. 1) and other simple ruthenium complexes, among them a Keggin-type heteropolyoxotungstate, previously used successfully for the deep oxidation of chlorophenols,[14] chloroolefins[15] and of cyclohexane to adipic acid,[16] that catalyzed also the oxidation of DBT and $DBTO_2$ into biphenylsultone ($DBTO_3$) in near quantitative yields using both monopersulfate and hydrogen peroxide as the oxidizing sources, in very mild conditions and in an aqueous–acetonitrile homogeneous phase; $DBTO_3$ easily undergoes hydrolysis into 2-(2′-hydroxybiphenyl)sulfonate (HBPS), which eventually desulfurizes to HBP and sulfuric acid. To the best of our knowledge, there is no previous literature report on oxidation of sulfones to sultones by chemical means.

Experimental

Materials: RuPcS was prepared by template synthesis starting from $RuCl_3{\cdot}3H_2O$, 4-sulfophthalic acid trisodium salt and urea.[14] Cobalt–sulfophthalocyanine (CoPcS),[17] *cis*-$[RuCl_2\{(CH_3)_2SO\}_4]$ (RuDMS),[18] $K_5[Ru(H_2O)PW_{11}O_{39}]$ (RuPW)[19] and biphenylsultone ($DBTO_3$)[20] were prepared by published procedures. FePcS, the organic substrates and chromatographic and spectroscopic standards were grade reagents from Aldrich.

A procedure for the catalytic oxidations is as follows. A water–acetonitrile (4 : 6) solution (8.5 ml) containing the substrates, 5 mM, and the metal catalysts, 1 mM, was stirred magnetically in a vial together with commercial Oxone® (corresponding to 0.05 M concentration of active oxygen as $KHSO_5$) or with hydrogen peroxide (0.05–0.5 M), as determined by iodometric titration. The reactions were carried out at 20 °C and were not affected by the presence of air. The progress of reaction was monitored by NMR and/or GC-MS. The products were identified by comparing their spectral data with those reported in the literature or of authentic compounds purposely prepared; conversion, yields and rates were reproducible to within 10–15%.

Organic analyses were performed on a HP 6890 GLC instrument equipped with FID, using a 30 m HP-5 capillary column (0.32 mm id; 0.25 film thick) with the injection port kept at 250 °C (carrier gas: He) on aliquots withdrawn with a microsyringe from the aqueous reaction mixtures either as such or diluted 1 : 10 with acetone. The identity of each product was confirmed by comparison of the fragmentation pattern in the mass spectra obtained with a MD 800 Fisons mass spectrometer operating in the electron ionization mode at 70 eV. To analyze the carboxylic acids as their isobutyl esters, the aqueous reaction mixtures were first evaporated under vacuum to small volumes, then refluxed for 3 h in the presence of a 20 : 1 excess 2-methyl-1-propanol and some drops of HCl_{conc}. Carbon dioxide evolved during the reactions was captured by an aqueous solution of freshly calibrated $Ba(OH)_2$ 0.0125 M and aliquots from the filtered solution were back-titrated with HCl 0.1 M. Sulfate ions, produced during the reactions, were analyzed by ionic chromatography with a DIONEX DX 100 instrument, equipped with IonPacAS4A-SC Analytical Column (4 × 250 mm).

The reactions were also followed by ^1H NMR on a Bruker Avance 300 MHz spectrometer equipped with a BBO 5 mm probe, by adding a small amount of D_2O to the reaction mixtures; water suppression was carried out by a presaturation sequence using a composite pulse (zgcppr Bruker sequence). A co-axial capillary tube containing 30 mM water (D_2O) solution of 3-(trimethylsilyl)propionic acid-2,2,3,3-d_4 sodium salt (TSP) was used as reference. The identity of each product and their quantitation were confirmed by comparison of the position and intensity of suitable signals after adding measured amounts of the pure compounds to the reaction mixtures. Average reproducibility of quantitative measurements was within 5%.

UV–visible spectra were measured out on a HP 8452A Diode Array, with a 200–820 nm spectral window.

ESI-MS (electrospray ionization MS) measurements were performed on a LCQ Advantage Thermofinnigan apparatus. Injections of the samples were done directly into the ESI detector at the flow rate of 6 μl min^{-1}.

The ionization voltage was set at +4500 V; capillary temperature was set at 180 C; capillary voltage and tube lens offset were set at −10 V and −50 V respectively. Instrument control and data acquisition were performed with a Dell Optiplex GX400 computer using XCALIBUR 1.2 Thermofinnigan software. The Mass Spectrometer was calibrated with reserpine obtained from Thermofinnigan and the ratio signal : noise was set 10 : 1.

Results and discussion

Our investigations on the oxidation of DBT and its oxidation products, *i.e.* $DBTO_2$, $DBTO_3$, HBPS and HBP were carried out at ambient temperature and an appropriate catalyst was always necessary in order to effectively promote the reactions. Conversions and product distributions for the examined catalysts, *i.e.* MPcS (M = Fe, Co, Ru), RuDMS and RuPW, did vary on a large scale and are shown in Tables 1 and 2, respectively. Initial work on the optimization of reaction conditions led to a standard protocol that was used throughout this study. This was as follows: 0.001 M catalyst and 0.005–0.01 M substrate in the acetonitrile–H_2O solution ($[H_2O]$ = 40 vol%) in the presence of 0.05 M oxone or 0.05–0.5 M H_2O_2; 20 °C temperature, and 24 h reaction time. At $[H_2O]$ around 40 vol% in the acetonitrile–H_2O mixture, the reaction system was homogeneous; at higher contents of acetonitrile the catalyst (and also the oxone oxidant) precipitated, whereas at lower contents it was the substrate (or the products) that separated from the solution. The chosen concentration range of the substrates (5–10 mM, corresponding to a sulfur content of 160–320

Table 1 Catalytic oxidation of dibenzothiophene and dibenzothiophene dioxide by monopersulfate[a]

		Dibenzothiophene				
		Composition of the reaction mixtures/mol%				
Catalyst	Time/h	DBT	$DBTO_2$	$DBTO_3$	HBP	Other[b]
None	1	47	53	—	—	—
	6	2	98	—	—	—
	24	—	100	—	—	—
CoPcS; RuDMS; RuPW	3	—	100	—	—	—
	24	—	100	—	—	—
FePcS	3	3	95	1	—	1
	24	—	92	2	—	6
RuPcS	1	—	88	1	4	7
	6	—	70	2	5	23
	26[c]	—	48	—	2	50

		Dibenzothiophene dioxide			
		Composition of the reaction mixtures/mol%			
Catalyst	Time/h	$DBTO_2$	$DBTO_3$	HBP	Other[b]
CoPcS	3	91	—	8	1
	24	87	—	3	10
FePcS	3	86	3	—	11
	24	81	4	—	15
RuPcS	3	65	—	3	32
	6	55	—	5	40
	24	40	1	9	50
RuPW	3	100	—	—	—
	24	98	2	—	—

[a] Catalyst, 1 mM; DBT or $DBTO_2$, 5 mM; $KHSO_5$, 0.1 M; in $H_2O : CH_3CN$ 4 : 6 (vol) 20 °C. [b] Mostly HBPS, together with minor amounts of CO_2 and products from the oxidative fission of the aromatic moieties (oxalic acid, benzoic acid). [c] CO_2 evolved: 11% (mol per mol of initial DBT). [d] No reaction in the absence of catalyst or in the presence of RuDMS, 1 mM (24 h).

ppm) is the normal concentration range of the effluent coming from conventional HDS treatment of fuels. Increasing the oxidant concentration led to significant changes in rates only in the case of the H_2O_2 oxidations. The increasing of the temperature (up to 60 °C) had little effect on the reaction rates and only led to an enhanced dismutation of the H_2O_2 oxidant. Lowering the catalyst concentration (to 0.1 mM) resulted in an early deactivation of the catalysts.

Biphasic oxidation of DBT (and $DBTO_2$) in water–dichloromethane (1 : 1) was completely unsuccessful, apart for the RuPcS catalyst, which exhibited a moderate activity for the oxidation of $DBTO_2$ by monopersulfate, with a 6% conversion after 24 h. Addition of conventional quaternary ammonium salt phase-transfer agents, such as trimethylcetyl ammonium hydrosulfate, did not improve yields and conversion rates; on the contrary, the catalytic systems led the alkyl chain of the phase transfer agents to a fast and complete oxidative degradation, thus making the experiments useless.

Oxidation with persulfate

The DBT persulfate-oxidation by metal catalysis involved initial fast formation of $DBTO_2$, probably *via* DBTO, however it was never detected in the reaction mixtures with only negligible over-consumption of monopersulfate, due to the metal-promoted dismutation of the oxidant to dioxygen and sulfate. In the absence of added catalyst, DBT was found to undergo oxidation to $DBTO_2$ with monopersulfate, although slow, with 100% conversion after *ca.* 8 h reaction at room temperature (see Fig. 2).

Table 2 Catalytic oxidation of dibenzothiophene and dibenzothiophene dioxide by hydrogen peroxide[a]

		Dibenzothiophene			
		Composition of the reaction mixture/mol%			
Catalyst	Time/h	DBT	$DBTO_2$	$DBTO_3$	Other[b]
RuPcS[d]	24	90	10	—	—
FePcS[d]	3	75	13	—	12
	24	15	24	—	61
FePcS	3	2	63	1	34
	6	—	62	2	36
	24[eh]	—	35	2	63

		Dibenzothiophene dioxide		
		Composition of the reaction mixture/mol%		
Catalyst	Time/h	$DBTO_2$	$DBTO_3$	Other[b]
FePcS	3	76	2	22
	6	70	2	28
	24[eh]	43	1	56

[a] Catalyst, 1 mM; DBT or $DBTO_2$, 10 mM; H_2O_2, 1 M; in $H_2O–CH_3CN$ 4 : 6 (vol) 20 °C. [b] Mostly HBPS, together with minor amounts of CO_2 and products from the oxidative fission of the aromatic moieties. [c] No reaction in the absence of catalyst or in the presence of CoPcS 1 mM (24 h). [d] In the same conditions, except that DBT, 5 mM, and H_2O_2, 0.1 M. [e] Reaction still running. [f] CO_2 evolved: 3% (mol per mol of initial DBT). [g] No reaction in the absence of catalyst or in the presence of CoPcS, RuPcS, RuPW, RuDMS or Fe(III) acetate, 1 mM or of FePcS, 0.1 mM (24 h). [h] Sulfate ions produced: 27% (mol per mol of initial $DBTO_2$).

Most of the metal complexes investigated were able to further oxidize $DBTO_2$ (Table 1). The reactions proceeded slowly, the most active catalyst being RuPcS, for which an initial oxidation rate of *ca.* 0.002 mM min^{-1} was estimated, *i.e.* almost three orders of magnitude smaller than the rate of the RuPcS-catalyzed transformation of DBT to $DBTO_2$ (*ca.* 1 mM min^{-1}). Although conversions at 24 h never exceeded 60%, the result was nevertheless interesting since under the same reaction conditions, "naked" ruthenium ions, arising upon the fast oxidation of the RuDMS catalyst, were found completely inactive for the further oxidation of $DBTO_2$.

A series of oxidation products were detected, including $DBTO_3$, HBPS and HBP, leading us to study in detail the reactions of each one of the above substrates. $DBTO_3$ was not always measurable by GC, since in aqueous media it

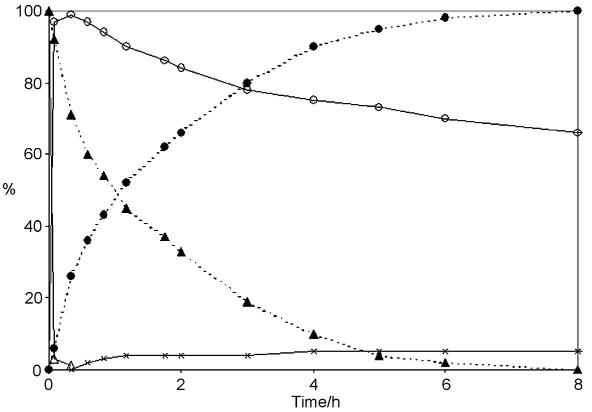

Fig. 2 Time course for the oxidation DBT, 5 mM, by $KHSO_5$, 0.05 M, in water–acetonitrile 40 : 60; 20 °C. Uncatalyzed reaction (---): DBT (filled triangles) $DBTO_2$ (filled circles). Reaction catalyzed by RuPcS, 1 mM (—): DBT (triangles) $DBTO_2$ (circles) HBP (crosses).

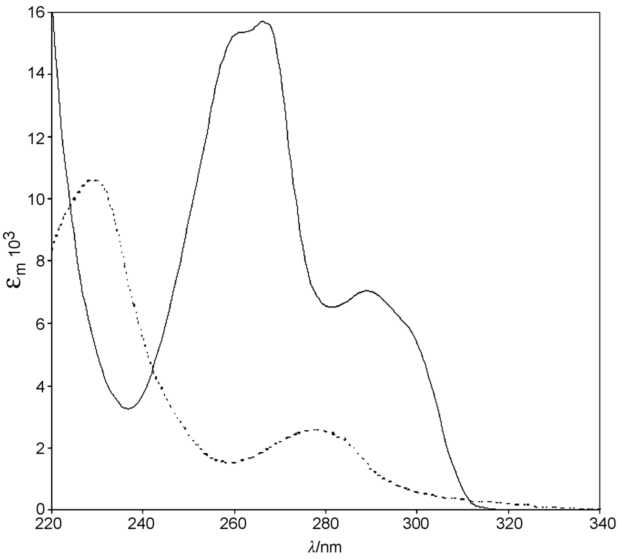

Fig. 3 UV spectra of $DBTO_3$in acetonitrile–water 6 : 4. As such, 0.5 mM at "pH" 6.4 (—) after treatment at 80 °C for 4 h in the presence of KOH 2.5 M; spectra were run at 2.5 mM concentration and at "pH 8" (---); 20 °C.

underwent more or less complete hydrolysis, depending upon pH and temperature. Hydrolysis was favored by alkaline media and indeed we proved that KOH water–acetonitrile solutions (0.25 M) led to 100% conversion of $DBTO_3$ to the corresponding sulfonate HBPS in few hours (at 80 °C). HBPS cannot be detected *via* GC, but dramatic changes were observed in the ^1H and ^{13}C NMR, UV and ESI spectra of the reaction mixtures. In particular, UV spectra exhibited the progressive disappearance of the distinctive absorptions of $DBTO_3$ at 265 and 290 nm, which were replaced by a new spectral pattern with a maximum at 275 nm, attributed to HBPS and clearly reminiscent of the reported UV spectra of 2-hydroxybiphenylsulfinate.[21] (Fig. 3)

Indeed, ESI-MS measurements (negative pattern) of the final reaction mixtures showed two intense peaks, at *m*/*z* 249, corresponding to the monopotassium cluster of HBPS, and at *m*/*z* 169 (−80), corresponding to the loss of SO_3, together with various other potassium cluster ions (Fig. 4).

The stability of $DBTO_3$ was also tested in acidic media ("pH" *ca.* 1, H_2SO_4 in aqueous acetonitrile), since under the reaction conditions oxone behaved as a strong Brønsted acid ("pH" *ca.* 2): fast hydrolysis to HBPS was again observed, although not complete, with an estimated equilibrium constant (UV spectra) of *ca.* 1.

Aqueous acetonitrile solutions of $DBTO_3$ and also those deriving from the complete alkaline hydrolysis of $DBTO_3$ to HBPS (after neutralization with H_2SO_4) were also tested for the catalytic oxidation by the MPcS complexes (M = Fe, Ru) at the same concentrations used in all the experiments: conversions up to 60% were observed after short times (1 h or less), with no product however detected by GC, apart small amounts of HBP, clearly indicating desulfurization. Furthermore, we noticed that HBP was quite unstable in the oxidizing media, by undergoing 100% oxidative degradation within very short times (< 1 h). Among the oxidation products, we were able to identify only CO_2 (11% mol per mol of initial substrate), oxalic (8%) and benzoic acid (4%), the latter two quantified as their isobutyl esters. The nature of the identified products clearly pointed to an effective oxidative fission of the aromatic moieties, in agreement with the previously reported general behavior of the persulfate/MPcS systems towards phenolic substrates (M = Fe,[22] Ru[14]), which typically underwent extensive oxidative fragmentation.

Oxidation with hydrogen peroxide

In contrast to persulfate, DBT was not affected (24 h) by H_2O_2 in the absence of catalysts. All the MPcS-catalyzed reactions with H_2O_2 suffered from heavy over-consumption of the oxidant, due to the dismutation of H_2O_2 to water and oxygen, and only with FePcS were acceptable results obtained. Test experiments showed indeed that the MPcS catalysts (1 mM in acetonitrile–water) behaved very differently as dismutating agents of H_2O_2 (1 M): whereas RuPcS promoted almost complete dismutation in less than 1 h, FePcS and CoPcS acted much slower, by at least one order of magnitude (specific runs, conducted in the presence of tetrafluoroboric acid at "pH" *ca.* 2, where dismutation was expected to slow down, did not show any significant improvement).

The various substrates examined, *i.e.* DBT, $DBTO_2$, $DBTO_3$ and HBP, were oxidized by the FePcS/H_2O_2 system at very different rates (Fig. 5): the $DTBO_2 \rightarrow DBTO_3$ oxidation

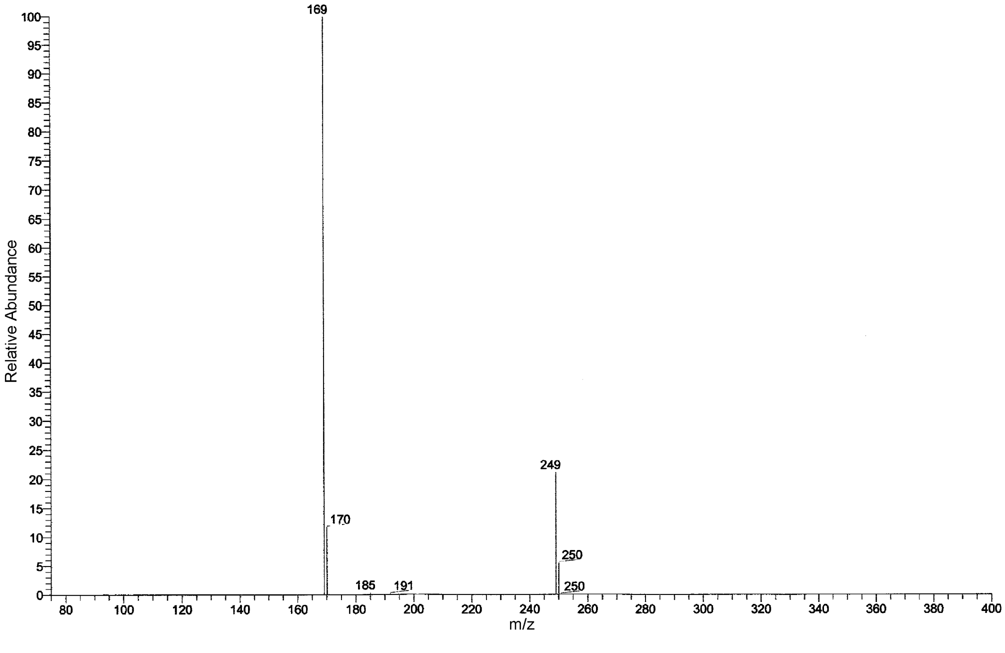

Fig. 4 ESI-MS spectrum of HBPS.

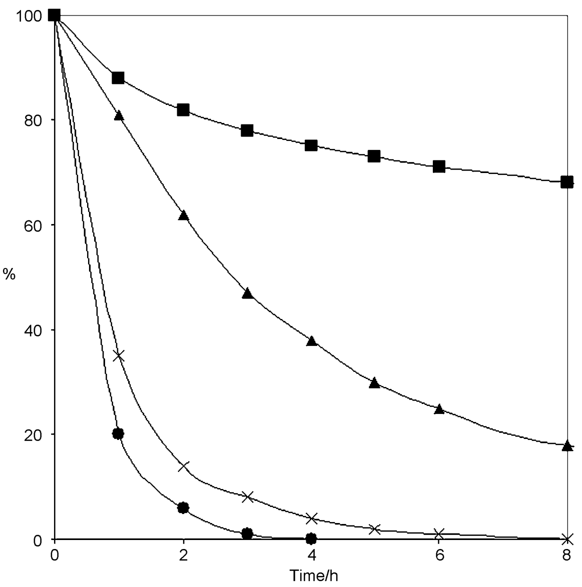

Fig. 5 Time course of the conversion of various substrates (10 mM) by oxidation with hydrogen peroxide (1 M) in the presence of FePcS (1 mM) catalyst; water–acetonitrile 40 : 60; 20 °C. DBT (circles) $DBTO_2$ (squares) $DBTO_3$ (triangles) HBP (crosses).

($t_{1/2}$, *ca.* 20 h) was the rate limiting step of the entire process, with the oxidation of both DBT and HBP being much faster ($t_{1/2}$, less than 1 h) and that of $DBTO_3$ somewhere in between ($t_{1/2}$, *ca.* three times faster than the latter). The mechanism of the H_2O_2 oxidations was closely related to that of the reactions conducted with oxone. For the H_2O_2-oxidations, also sulfate ions, produced by the probable desulfurization of the substrate, could be measured, which accounted for 27% (mol per mol of substrate) it was however uncertain whether all the sulfate came from the desulfurization of the substrate, since blank runs conducted on FePcS/H_2O_2 system in the absence of added substrates showed significant production of sulfate upon direct desulfurization of the PcS ring.

Conclusion

A survey of the recent literature showed that liquid-phase oxidations of DBT by chemical means only led to $DBTO_2$, whereas enzymatic catalysts were able to effectively desulfurize the substrate in the presence of molecular oxygen. Although the present catalytic system should be tested in the presence of a commercial diesel sample to understand the action of the hydrocarbon molecules on the catalytic activity, the study demonstrated that metal catalyzed oxidation of DBT with common peroxidic oxidants was feasible, with formation of HBPS and also desulfurization products, such as HBP, in good yields and under mild conditions. Oxidation of DBT occurred in aqueous acetonitrile, either with H_2O_2 and catalyzed by FePcS or with oxone and catalyzed by RuPcS, at substrate loading down to 160 ppm of sulfur content (w/w). In the presence of oxone RuPcS was more effective than FePcS, whereas with H_2O_2 the opposite was found; this poorer performance was however not due to an intrinsic, poorer reactivity of the RuPcS/H_2O_2 system, but to the fact that the complex promoted a very effective dismutation of the oxidant, thus making less profitable RuPcS, if compared to FePcS. The oxidation pathway for the present reactions consisted in the conventional multistep process (Fig. 6), controlled, as expected, by the slow oxygenation of $DBTO_2$ to $DBTO_3$.

The mild conditions used may lead to an attractive, environmentally acceptable procedure for the one step transformation of DBT into desulfurized products or the sulfonate derivative HBPS, insoluble in organic media. Effective biphasic oxidation, which could allow easier product separation, was not achieved in the present work: novel phase transfer agents, more resistant to the oxidizing media could make viable this crucial step.

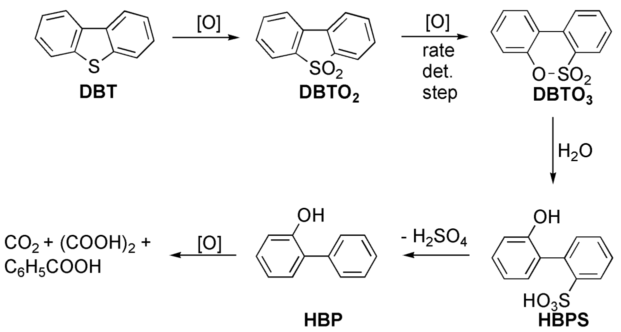

Fig. 6 Proposed reaction pathway for the oxidation of DBT.

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