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 sulfur-

ous 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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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 sites⁶ 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 (DBTO₂).⁹⁻¹¹ Deep oxidations of DBT are reported to occur upon sonication, yielding desulfurized products, such as hydroxy- and dihy-droxy-dibenzothiophenes,¹² or upon exposure to sunlight, to give acidic photoproducts, such as 2-sulfobenzoic acid.

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 chloroolefins¹⁵ and of cyclohexane to adipic acid,¹⁶ that catalyzed also the oxidation of DBT and DBTO₂ into biphenylsultone (DBTO₃) 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; DBTO₃ easily undergoes hydrolysis into 2-(2'-hydroxy-biphenyl)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 RuCl₃·3H₂O, 4-sulfophthalic acid trisodium salt and urea.¹⁴ Cobalt–sulfophthalocyanine (CoPcS),¹⁷ *cis*-[RuCl₂{(CH₃)₂-SO}₄] (RuDMS),¹⁸ K₅[Ru(H₂O)PW₁₁O₃₉] (RuPW)¹⁹ and biphenylsultone (DBTO₃)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 KHSO₅) 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-d₄ 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 μ l 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. DBTO₂, DBTO₃, 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-H₂O solution ([H₂O] = 40 vol%) in the presence of 0.05 M oxone or 0.05-0.5 M H₂O₂; 20 °C temperature, and 24 h reaction time. At [H₂O] around 40 vol% in the acetonitrile-H₂O 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

Catalyst	Time/ h	Dibenzothiophene						
		Composition of the reaction mixtures/mol%						
		DBT	DBTO ₂	DBTO ₃	HBP	Other ^b		
None	1	47	53	_	_	_		
	6	2	98	_	_	_		
	24	_	100	_	_	_		
CoPcS;	3	_	100	_	_	_		
RuDMS; RuPW								
	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		

Catalyst	Time/ h	Composition of the reaction mixtures/mol%					
		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 DBTO₂, 5 mM; KHSO₅, 0.1 M; in H₂O : CH₃CN 4 : 6 (vol) 20 °C. ^b Mostly HBPS, together with minor amounts of CO₂ and products from the oxidative fission of the aromatic moieties (oxalic acid, benzoic acid). ^c CO₂ 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 H₂O₂ 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 H2O2 oxidant. Lowering the catalyst concentration (to 0.1 mM) resulted in an early deactivation of the catalysts.

Biphasic oxidation of DBT (and DBTO₂) in water-dichloromethane (1:1) was completely unsuccessful, apart for the RuPcS catalyst, which exhibited a moderate activity for the oxidation of DBTO₂ 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 DBTO2, probably via DBTO, however it was never detected in the reaction mixtures with only negligible over-consumption of monopersulfate, due to the metalpromoted dismutation of the oxidant to dioxygen and sulfate. In the absence of added catalyst, DBT was found to undergo oxidation to DBTO₂ with monopersulfate, although slow, with 100% conversion after ca. 8 h reaction at room temperature (see Fig. 2).

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Table 2 Catalytic oxidation of dibenzothiophene and dibenzothiophene dioxide by hydrogen peroxide

		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		
		Dibe	nzothiophene	dioxide			
		Composition of the reaction mixture/mol%					
Catalyst	Time/h	DBT	°O ₂	DBTO ₃	Other ^b		
FePcS	3	76		2	22		
	6	70		2	28		

^a Catalyst, 1 mM; DBT or DBTO₂, 10 mM; H₂O₂, 1 M; in H₂O-CH₃CN 4 : 6 (vol) 20 °C. ^b Mostly HBPS, together with minor amounts of CO₂ 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 H₂O₂, 0.1 M. ^e Reaction still running. ^f CO₂ evolved: 3% (mol per mol of initial DBT). 9 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 DBTO₂).

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 $2\Delta^{eh}$

Most of the metal complexes investigated were able to further oxidize DBTO₂ (Table 1). The reactions proceeded slowly, the most active catalyst being RuPcS, for which an initial oxidation rate of ca. 0.002 m \overline{M} min⁻¹ was estimated, i.e. almost three orders of magnitude smaller than the rate of the RuPcS-catalyzed transformation of DBT to DBTO₂ (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 DBTO₂.

A series of oxidation products were detected, including DBTO₃, HBPS and HBP, leading us to study in detail the reactions of each one of the above substrates. DBTO3 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) DBTO₂ (filled circles). Reaction catalyzed by RuPcS, 1 mM (-): DBT (triangles) DBTO₂ (circles) HBP (crosses).



Fig. 3 UV spectra of DBTO₃in 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 DBTO₃ 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 ¹³C NMR, UV and ESI spectra of the reaction mixtures. In particular, UV spectra exhibited the progressive disappearance of the distinctive absorptions of DBTO₃ 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 SO₃, together with various other potassium cluster ions (Fig. 4).

The stability of DBTO₃ was also tested in acidic media ("pH" ca. 1, H₂SO₄ 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 DBTO₃ and also those deriving from the complete alkaline hydrolysis of DBTO₃ to HBPS (after neutralization with H₂SO₄) 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 CO2 (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, DBTO₂, DBTO₃ and HBP, were oxidized by the FePcS/H₂O₂ system at very different rates (Fig. 5): the DTBO₂ \rightarrow DBTO₃ 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) DBTO₂ (squares) DBTO₃ (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 DBTO₃ somewhere in between $(t_{1/2}, ca. three times faster than the latter). The mechanism of the H₂O₂ oxidations was closely related to that of the reactions conducted with oxone. For the H₂O₂-oxidations, also sulfate ions, produced by the probable desulfurization of the substrate, could be measured, which accounted for 27% (mol per mol of substrate) it was however uncertain whether all the sulfate came from the desulfurization of the substrate, since blank runs conducted on FePcS/H₂O₂ system in the absence of added substrates showed significant production of sulfate upon direct desulfurization of the PcS ring.$

Conclusion

A survey of the recent literature showed that liquid-phase oxidations of DBT by chemical means only led to DBTO₂, 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 H₂O₂ 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 H₂O₂ 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 DBTO₂ to DBTO₃.

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



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

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.

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