Oxidation of Polycyclic Aromatic Hydrocarbons Catalyzed by Iron Tetrasulfophthalocyanine FePcS: Inverse Isotope Effects and Oxygen Labeling Studies

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Iron(III) tetrasulfophthalocyanine (FePcS) was shown to catalyze the oxidation of polycyclic aromatic hydrocarbons by H_2O_2. Benzo[*a*]pyrene and anthracene were converted to the corresponding quinones while biphenyl-2,2′-dicarboxylic acid was the main product of phenanthrene oxidation. The mechanism of the anthracene oxidation by H_2O_2 in the presence of FePcS or by $KHSO_5$ with iron(III) *meso*-tetrakis(3,5-disulfonatomesityl)porphyrin (FeTMPS) (see Figure 1 for catalyst structures) has been investigated in details by using kinetic isotope effects (KIEs) and ^{18}O labeling studies. KIEs measured on the substrate consumption in the competitive oxidation of [H_{10}]anthracene and [D_{10}]anthracene by FePcS/H_2O_2 and FeTMPS/$KHSO_5$ were essentially the same, 0.75 ± 0.02 and 0.76 ± 0.06, respectively. These inverse KIEs on the first oxidation step can be explained by the sp^2-to-sp^3 hybridization change during the addition of an electrophilic oxoiron complex to the sp^2 carbon center of anthracene to form a σ adduct (this inverse KIE being enhanced by stronger stacking interactions between the perdeuterated substrate with the macrocyclic catalyst). Although the first oxidation step seems to be the same, different distribution of the oxidation products of anthracene and very different ^{18}O incorporation into anthrone and anthraquinone in catalytic oxidations performed in the presence of $H_2{}^{18}O$ suggested that different active species should be responsible for anthracene oxidation in both catalytic systems. All the results obtained are compatible with an involvement of $TMPSFe^{V}=O$ (or $TMPS^{+}Fe^{IV}=O$), having two redox equivalents above the iron(III) state of the metalloporphyrin precursor, while $PcSFe^{IV}=O$ (one redox equivalent above Fe^{III} state of FePcS) was proposed to be the active species in the metallophthalocyanine-based system.

Introduction

Polycyclic aromatic hydrocarbons (PAH) belong to environmental pollutants because of their rather slow biodegradation. PAHs can be metabolized by bacteria, fungi or algae. Three main degradation pathways have been identified for the microbial catabolism of polycyclic aromatic hydrocarbons[1]. Cytochrome P-450 monooxygenases catalyze the formation of arene oxides, which are then transformed to phenol or epoxy-diol derivatives. Ligninases are capable of oxidizing PAH to quinones followed by ring cleavage[2]. For example, benzo[*a*]pyrene was oxidized to a mixture of 1,6-, 3,6- and 6,12-quinones[3], pyrene to 1,6- and 1,8-quinones[4] and anthracene to 9,10-anthraquinone[2]. The third enzymatic degradation process involves dioxygenase enzymes to incorporate both atoms of molecular oxygen into the aromatic ring to form *cis*-dihydrodiols. After a dehydrogenase-catalyzed rearomatization to produce catechols, a subsequent enzymatic cleavage by intradiol or extradiol dioxygenases gives *cis,cis*-muconic acid or 2-hydroxymuconic semialdehyde as products of aromatic cycle cleavage, respectively[5]. Although biodegradation of PAHs is the major decontamination process, along with photochemical oxidation with dioxygen[6], microorganisms capable of rapidly and efficiently mineralizing recalcitrant and potentially carcinogenic PAHs needs to be found[1]. Chemical oxidation of PAH[7] needs elevated temperatures and/or powerful oxidants, e.g. chromium compounds which constitute environmental problems. For example, phenanthrene has been oxidized to phenanthrenequinone by CrO_3 at 55°C (yield 80%)[8], by the system $Ce^{IV}/H_2SO_4/(NH_4)_2SO_4$ at 50°C (yield 42%)[9], by $KMnO_4/Al_2O_3/H_5IO_6$ (yield 25%)[10]. Arenes can be oxidized to quinones by H_2O_2/hexafluoroacetone at 70°C[11]. In this latter case, biphenyl-2,2′-dicarboxylic acid was the only isolated oxidation product of phenanthrene[11]. Obviously, there is a need for environmental-friendly chemical catalysts to oxidize PAH. An alternative approach using biomimetic metalloporphyrin catalysts[12] has been shown to be useful in the oxidation of 2-methylnaphthalene[12a]. Phenanthrene and naphthalene were oxidized by a porphyrinruthenium/2,6-dichloropyridine *N*-oxide system to give the corresponding quinones with 40% and 29% yields, respectively[13]. Recently, the oxidation of naphthalene and methylnaphthalenes by peracetic

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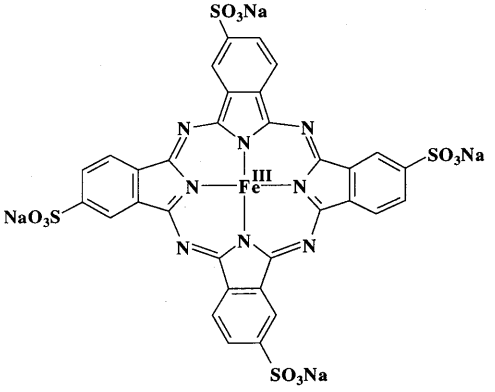
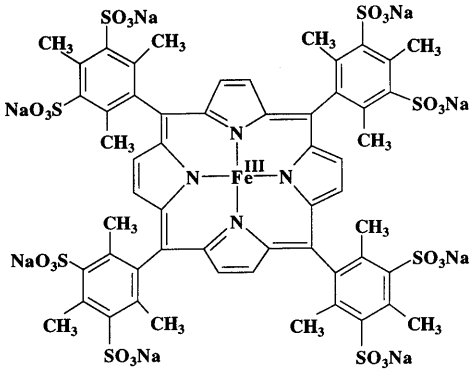
acid catalyzed by octanitrophthalocyanine Mn^{III} and Fe^{II} complexes has been reported[14].

We recently developed a new efficient catalytic system for the oxidative degradation of polychlorinated phenols based on the association of iron(III) or manganese(III) complexes of tetrasulfophthalocyanine (FePcS, MnPcS) and the rather inexpensive and "green" oxidant H_2O_2[15][16]. This biomimetic system is able to cleave the aromatic cycle of 2,4,6-trichlorophenol with the formation of chloromaleic acid as the main product[15]. Besides FePcS and MnPcS, CoPcS is also highly efficient in the oxidation of catechols[17]. Having on hands these efficient catalysts for the oxidation of recalcitrant pollutants such as chlorinated phenols, we decided to investigate the activity of these catalysts in the oxidation of other poorly biodegradable molecules. Here we report the catalytic oxidation of polycondensed aromatics (mainly anthracene, but also phenanthrene and benzo[*a*]pyrene) by hydrogen peroxide or potassium monopersulfate ($KHSO_5$) and FePcS as catalyst [FeTMPS, a water-soluble iron(III) porphyrin, was also used for comparison]. Detailed mechanistic studies involving kinetic isotope effects (KIEs) and ^{18}O labeling experiments are also reported.

Figure 1. Structures of iron(III) complexes of tetrasulfophthalocyanine (FePcS) and *meso*-tetrakis(3,5-disulfonatomesityl)porphyrin



Iron tetrasulfophthalocyanine (FePcS)



Iron meso-tetrakis(3,5-disulfonatomesityl)porphyrin (FeTMPS)

Results

Products and Reactivity Order in PAH Oxidations by FePcS/H_2O_2

We checked the oxidations of benzo[*a*]pyrene, phenanthrene and anthracene, performed in a MeCN/H_2O mixture (3:1, v/v) using $KHSO_5$ and H_2O_2 as oxidants. The final concentrations of oxidant and substrate were 5 mM and 1 mM, respectively. The catalyst concentrations were 10 μM, 37 μM and 100 μM corresponding to 1, 3.7 and 10% catalyst/substrate ratios, respectively. The data of Table 1 indicated that FePcS was also an efficient catalyst for the oxidation of these polyaromatic hydrocarbons. The oxidation of benzo[*a*]pyrene by FePcS/$KHSO_5$ (run 1) and by FePcS/H_2O_2 (run 4) at pH = 7 was complete within in a few minutes leading to an orange material isolated by precipitation with water. DCI-CH_4 mass spectrometry analysis gave peaks at 282 (M^+, 100), 254 [$(M - CO)^+$, 17.4], 226 [$(M - 2\ CO)^+$, 17.4] indicating the final product was a quinone (or a mixture of quinone isomers) with a molecular weight equal to 282. Three components were isolated by dry column chromatography (neutral Al_2O_3, benzene) after oxidation of benzo[*a*]pyrene in conditions used for run 4 of Table 1 and characterized by UV spectroscopy according to ref.[18] (Scheme 1). The UV/Vis spectra for all three quinones were in an excellent agreement with the data previously published[18]. Based on reported extinction coefficients, the distribution of quinones was as follows: 6,12-benzo[*a*]pyrenedione (32%, first eluted product from column), 1,6- benzo[*a*]pyrenedione (44%, second eluted product) and 3,6- benzo[*a*]pyrenedione (24%, third eluted product). The total yield for all three quinones was quantitative

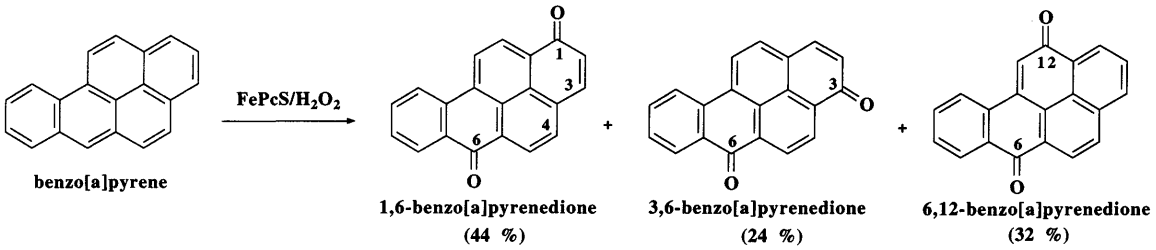
Table 1. Oxidation of polyaromatic hydrocarbons PAH by H_2O_2 and $KHSO_5$ catalyzed by sulfonated phthalocyanineiron(III) FePcS[a]

Run	Oxidant	pH	% Cat./Sub.	Conversion [%]		
				1 min	5 min	60 min
		Benzo[*a*]pyrene oxidation				
1	$KHSO_5$	2	1	50	97	100
2	$KHSO_5$	7	1	14	41	70
3	H_2O_2	7	1	11	20	20
4	H_2O_2	7	3.7	43	100	100
		Anthracene oxidation				
5	H_2O_2	4.4	10	12	40	96
6	H_2O_2	7	10	100		
7	H_2O_2	7	3.7	57	74	86
8	H_2O_2	7	1	15	28	32
		Anthracene oxidation by FeTMPS/$KHSO_5$				
9	$KHSO_5$	7	3.7	11	33	100
		Phenanthrene oxidation				
10	$KHSO_5$	7	3.7	28	40	64
11	H_2O_2	5.3	3.7	10	24	35
12	H_2O_2	5.3	10	n.d.	n.d.	66
13	H_2O_2	5.5	10	32	46	64
14	H_2O_2	5.9	10	n.d.	45	60
15	H_2O_2	4.4	10	n.d.	24	80

[a] n.d.: not determined.

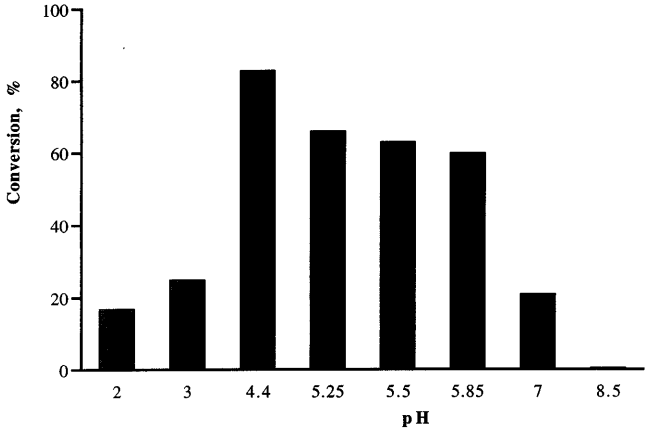
The H_2O_2 oxidation of phenanthrene is pH-dependent. Using a 10% catalyst/substrate ratio the highest conversion of phenanthrene was obtained at pH = 4.4 (conversion be-

Scheme 1. Oxidation products of benzo[*a*]pyrene by $FePcS/H_2O_2$



ing rather low at pH = 7) (Figure 2). But it should be noted that anthracene was quickly and completely oxidized within 1 min at pH = 7 (Table 1, run 6) while 1 hour was necessary to reach 96% conversion at pH = 4.4 (the pH optimum for phenanthrene). At pH = 7 the order of substrate reactivity was in agreement with oxidation potentials: benzo[*a*]pyrene > anthracene > phenanthrene (the ionization potentials being 7.2, 7.4 and 8.1 eV, respectively[2]).

Figure 2. pH dependence of phenanthrene oxidation by FePcS/H_2O_2[a]



[a] Reaction conditions: [catalyst] = 0.1 mM, [oxidant] = 5 mM, [substrate] = 1 mM, acetonitrile/50 mM phosphate buffer at pH = 7 (3:1, v/v). Reaction time 60 min.

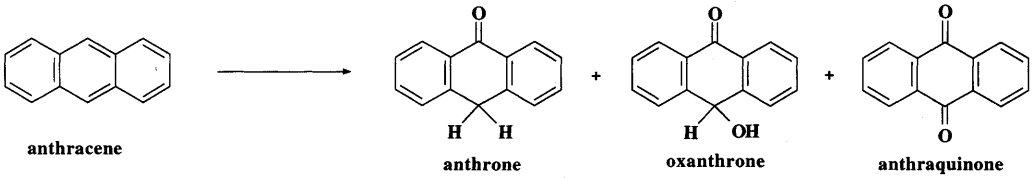
The FePcS-catalyzed oxidation of anthracene by H_2O_2 resulted in the formation of anthrone (tautomeric form of 9-hydroxyanthracene), oxanthrone (tautomeric form of anthrahydroquinone) and anthraquinone (Scheme 2). The yields of oxanthrone (5%) and anthraquinone (25%) were determined after 1 h by HPLC using calibration curve and molar extintion coefficients obtained with authentic samples.

Biphenyl-2,2′-dicarboxylic acid (product of cleavage of one aromatic cycle) was the main oxidation product of phenanthrene, 9,10-phenanthrenequinone being the second main product. Three other minor products of the oxidative degradation of phenanthrene were also identified by GC-MS analysis: 2-formyl-2′-hydroxybiphenyl, 2-carboxy-2′-hydroxybiphenyl and 2,2′-biphenylcarbolactone (Scheme 3). So, the $FePcS/H_2O_2$ system is able to cleave the aromatic cycle of phenanthrene and to perform oxidative decarboxylation.

Oxidation of Anthracene by $FeTMPS/KHSO_5$

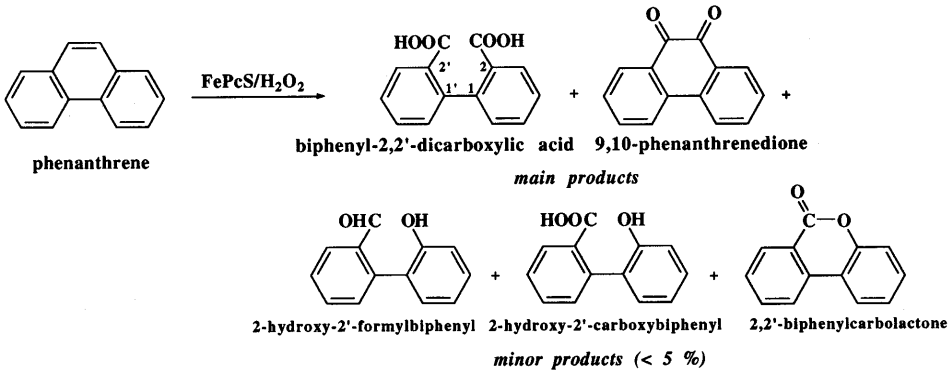
We also checked the oxidation of anthracene by $FeTMPS/KHSO_5$ performed in an MeCN/25 mM phosphate buffer mixture (3:1, v/v) at pH = 7. The concentrations of oxidant, substrate and catalyst were 5 mM, 1 mM and 37 μM, respectively. The anthracene conversion was complete after 60 min (run 9, Table 1). The yields of oxanthrone and anthraquinone were determined by HPLC. Differing from the $FePcS/H_2O_2$ mediated oxidation, the main product with $FeTMPS/KHSO_5$ was oxanthrone (yield by HPLC = 60%), while only 3% of anthraquinone were found. Isolation of reaction products from a large scale anthracene oxidation by $FeTMPS/KHSO_5$ followed by NMR analysis gave 43% yield for oxanthrone, 16% yield for anthraquinone and 14% yield of non-identified compounds (probably coupling products). A partial oxidation of oxanthrone to anthraquinone might have occured during the sample preparation for NMR analysis, explaining the discrepancy with the HPLC analysis of the reaction mixture. This rather unexpected result, oxanthrone, an easily oxidizable compound, as main reaction product in the presence of strong oxidants, stimulated us for a detailed mechanistic study of anthracene oxidation by both catalytic systems, $FePcS/H_2O_2$ and $FeTMPS/KHSO_5$.

Scheme 2. Oxidation products of anthracene by $FePcS/H_2O_2$ or $FeTMPS/KHSO_5$



Conversion: 79 % (30 min)	**$FePcS/H_2O_2$**	**< 5 %**	**5 %**	**21 %**
Conversion: 100 % (30 min)	**$FeTMPS/KHSO_5$**	**< 5 %**	**43 %**	**16 %**

Scheme 3. Oxidation products of phenanthrene by $FePcS/H_2O_2$



Stability of Anthrone, Oxanthrone and Anthraquinone in the Presence of $FePcS/H_2O_2$ and $FeTMPS/KHSO_5$

In these experiments we used the same reaction conditions as those for anthracene oxidation: a MeCN/50 mM phosphate buffer pH = 7 reaction medium (3:1, v/v), [catalyst] = 37 μM, [oxidant] = 5 mM, [substrate] = 1 mM, except for anthraquinone (its concentration was reduced to 0.5 mM because of its low solubility in the reaction mixture). Under these reaction conditions the conversions of anthrone in the presence of $FePcS/H_2O_2$ and $FeTMPS/KHSO_5$ were 23% and 38%, respectively, after 1 h, indicating that anthrone oxidation was slightly faster with $FePcS/KHSO_5$. Oxanthrone was easily oxidized to anthraquinone by $FePcS/H_2O_2$: the conversion was 90% after only 5 min. Again, oxanthrone was relatively stable with $FeTMPS/KHSO_5$: the conversions were only 18 and 23% after 30 and 60 min, respectively. Finally, we checked that anthraquinone was stable in both catalytic systems. There was no observable conversion after 60 min with $FeTMPS/KHSO_5$ and only 10% with $FePcS/H_2O_2$. These results on stability of products of anthracene oxidation were in good agreement with the composition of the reaction products for both catalytic systems.

Method of Determination of Kinetic Isotope Effects

Kinetic isotope effects (KIEs) can be determined in intra- or intermolecular competitive experiments by the analysis of the ratios of reaction products resulting from C−H versus C−D bond transformations. Such analyses are reliable when the oxidation products, different only in their isotopic substitution, are primary oxidation products and are stable in the reaction conditions. Since this is not a case in PAH oxidations by $FePcS/H_2O_2$ system we decided to determine the KIE values by analyzing of the competitive consumption of the deuterated versus the non-deuterated substrate. In this case intermolecular KIE values of the initial oxidation reaction can be obtained. In order to determine these KIEs concentrations of labeled and unlabeled substrates should be determined before and after the oxidation reaction by monitoring the isotopic composition of the initial reaction mixture, the substrate conversion and the isotopic composition of the remaining substrate after reaction. Isotopic compositions of substrates were determined by GC-MS analyses and substrate conversions were obtained by HPLC analyses (see Experimental Section). Equations to calculate KIEs depend on a reaction order in substrate[19]. When the reaction is first order in substrate KIEs can be determined from equation (1) where a_H°, a_D° and a_H, a_D denote initial and current substrate concentrations of H-labeled and D-labeled substrates, respectively.

$$k_H/k_D = \log (a_H/a_H^\circ) / \log (a_D/a_D^\circ) \quad (1)$$

Determination of the Reaction Order for the Substrate in Anthracene Oxidation by $FePcS/H_2O_2$

The reaction order in anthracene was determined with concentrations of H_2O_2, anthracene and FePcS being 5 mM, 1 mM and 37 μM, respectively. The reactions were carried out in an MeCN/50 mM phosphate buffer mixture at pH = 7 (3:1, v/v). Under these conditions the catalytic reaction follows a first-order kinetic in substrate at least for 2 times the reaction half-time and KIEs could be then determined according to equation (1).

KIEs in Anthracene and Phenanthrene Oxidation by $FePcS/H_2O_2$ and $FeTMPS/KHSO_5$

Analysis of the reaction mixture after 3−5 min of reaction (conversions being 40−60%) indicated a preferential consumption of $[D_{10}]$anthracene corresponding to an inverse isotope effect. The kinetic isotope effect in anthracene oxidation by the $FePcS/H_2O_2$ system was determined to be equal to 0.75 ± 0.02. Oxidation of anthracene by $FeTMPS/KHSO_5$ presented the same isotope effect of 0.76 ± 0.06 (Table 2). In contrast, oxidation of phenanthrene by both catalytic systems proceeds with no significant isotope effect: 0.96 ± 0.04 and 1.02 ± 0.01 for $FePcS/H_2O_2$ and $FeTMPS/KHSO_5$, respectively (Table 2).

In order to find the origin of this inverse isotope effects we prepared 9,10-dideuterioanthracene and determined the KIE value in the competitive oxidation of the mixture of 9,10-dideuterioanthracene and $[H_{10}]$anthracene. In this latter case the KIE value were 0.90 ± 0.05 and 0.95 ± 0.01 with the $FePcS/H_2O_2$ and $FeTMPS/KHSO_5$ systems, respectively.

Table 2. Kinetic isotope effect[a] in anthracene and phenanthrene oxidation by $FePcS/H_2O_2$ and $FeTMPS/KHSO_5$ at 20°C

Catalytic system	KIE in the competitive oxidation of [H_{10}]anthracene/[D_{10}]anthracene[b] ([H_{10}]anthracene/9,10-[D_2]anthracene)	[H_{10}]phenanthrene/[D_{10}]phenanthrene[c]
$FePcS/H_2O_2$	0.75 ± 0.02 (0.90 ± 0.05)	0.96 ± 0.04
FeTMPS/$KHSO_5$	0.76 ± 0.06 (0.95 ± 0.01)	1.02 ± 0.01

[a] These data are the mean values obtained from 3 independent oxidation reactions. – [b] Reaction conditions: [catalyst] = 37 μM, [oxidant] = 5 mM, [substrate] = 1 mM, MeCN/50 mM phosphate buffer pH = 7 (3:1, v/v). – [c] Reaction conditions: [catalyst] = 100 μM, [oxidant] = 5 mM, [substrate] = 1 mM, MeCN/33.3 mM phosphate buffer pH = 4.6 (1:1, v/v).

Analysis of Isotopic Composition of Products of Anthracene Oxidation

Anthrone, oxanthrone and anthraquinone were identified as oxidation products of anthracene by NMR and GC-MS techniques. GC-MS analysis of the reaction mixture indicated that anthrone, the primary oxidation product, was enriched in the deuterated derivative as expected from the inverse isotope effect on the first step of anthracene oxidation. In contrast, anthraquinone, a second oxidation product, was enriched in unlabeled product indicating a KIE value > 1 during the oxidation of anthrone to this quinone. Oxanthrone was unstable under GC-MS analysis conditions and its isotopic composition could not be determined. The molecular peak of deuterated anthrone formed after 3 min of reaction was 202 corresponding to a [D_8]-containing molecule, not a [D_9]-molecule as expected for 9-hydroxyanthracene. This result suggested that the equilibrium between the two tautomeric forms, anthrone and 9-hydroxyanthracene, was rather fast (Scheme 4). Consequently, a putative σ adduct with a Fe–O–arene bond, which should stabilize the 9-hydroxyanthracene tautomer, could not be a long-lived intermediate as previously observed in the metalloporphyrin-catalyzed oxidation of 2-methylnapthalene[12a].

^{18}O-Labeling Experiments

Oxidations of organic substrates catalyzed by metalloporphyrin[12][20][21] and metallophthalocyanine[16] complexes in the presence of ^{18}O-labeled water or dioxygen provided valueable mechanistic information. In order to investigate the mechanism of these catalytic PAH oxidations we performed the oxidation of anthracene by $FePcS/H_2O_2$ and $FeTMPS/KHSO_5$ in reaction mixtures containing ^{18}O-labeled water. In control experiments we checked that light oxygen atoms of anthraquinone did not exchange with heavy oxygen atoms of ^{18}O-labeled water under the used reaction conditions, i.e. a mixture of acetonitrile/50mM phosphate buffer (3:1, v/v) at pH = 7. Also, $KHSO_5$ itself does not exchange its oxygen atoms with water[20c]. FePcS-mediated oxidations of anthracene were performed under standard conditions (run 7 of Table 1) either under air or under nitrogen, using a 50:50 mixture of [H_{10}]anthracene and [D_{10}]anthracene. The oxygen atom distribution was analyzed in both deuterated and non-deuterated products for each experiment. In all cases, the oxygen atom distribution for a defined product was exactly the same. For example, the ^{18}O incorporation into anthraquinone was followed by determination of the molecular ion percentages at 208/216 [M], 210/218 [M + 2] and 212/220 [M + 4] corresponding to the incorporation of none, one or two ^{18}O oxygen atoms in [H_8]anthraquinone and [D_8]anthraquinone, respectively. In both cases, under air or under nitrogen, anthrone, the primary oxidation product, contained only a light oxygen atom. This result indicates that this oxygen atom originated from H_2O_2, the non-labeled oxidant. In contrast, both ^{16}O and ^{18}O atoms were incorporated into anthraquinone. When the reaction was performed under air, the molecular cluster consisted of M (68%) and M + 2 (32%) peaks, meaning that the ^{18}O atom was unambiguously only located in one carbonyl group of this quinone. If ^{18}O would occupied both carbonyl positions, the molecular cluster would have consisted on three peaks: M, M + 2 and M + 4. So, anthraquinone contained 100% of ^{16}O in one carbonyl position, 36% of ^{16}O and 64% of ^{18}O in another one (Figure 3). When the reaction was performed under nitrogen, again, only two peaks were found in the molecular cluster: M (56%) and M + 2 (44%). Consequently, ^{16}O incorporation in one carbonyl position was complete, another carbonyl position was enriched with heavy oxygen: 12% of ^{16}O and 88% of ^{18}O (Figure 3). This more significant incorporation of ^{18}O at the second carbonyl position produced in the absence of dioxygen suggests a possibility of O_2 involvement into oxidation pathway from anthrone to anthraquinone.

We also studied the ^{18}O incorporation from labeled water into the oxidation products of anthracene mediated by $FeTMPS/KHSO_5$. In this latter case, the mass spectrum of anthrone indicated the incorporation of ^{18}O atom, unlike with the $FePcS/H_2O_2$ oxidation. The percentage of ^{18}O found in anthrone was 63%, ^{16}O incorporation being only 37% (Figure 3). The MS molecular cluster of anthraquinone consisted of 3 peaks: M (16%), M + 2 (59%) and M

Scheme 4. Deuterium exchange during the formation of anthrone in aqueous medium

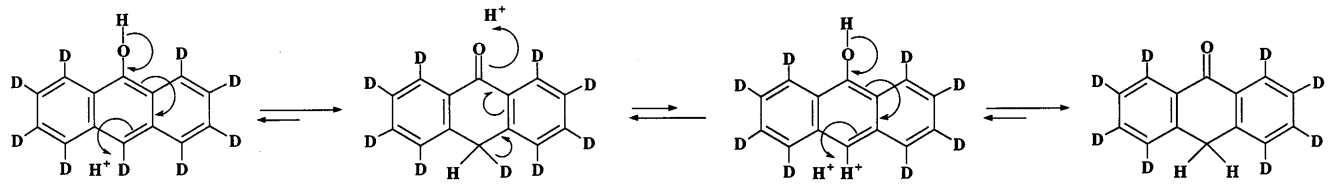
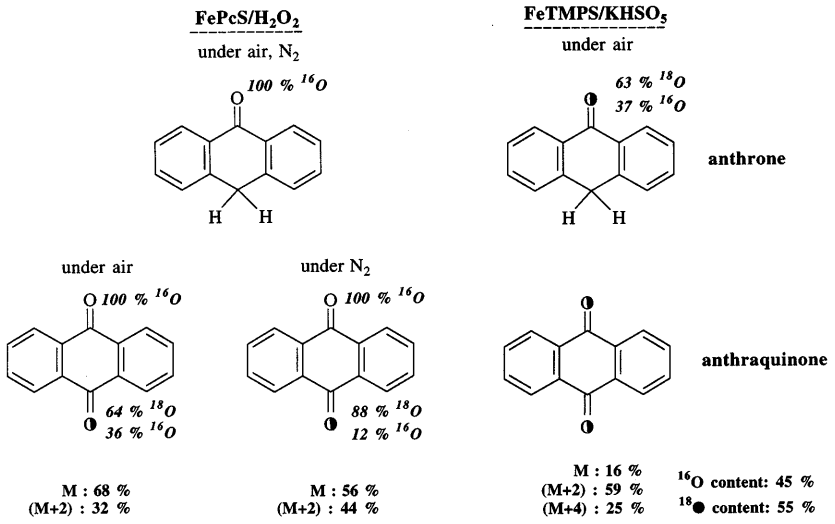


Figure 3. ^{18}O incorporation into anthrone and anthraquinone during the oxidation of anthracene by $FePcS/H_2O_2$ and $FeTMPS/KHSO_5$ in the presence of $H_2{}^{18}O$



+ 4 (25%), indicating that ^{18}O was incorporated in both carbonyl groups of the quinone (the amount of ^{16}O and ^{18}O being 45 and 55%, respectively) (Figure 3). From these labeled water experiments we concluded that active species involved in the oxidation of anthracene by $FePcS/H_2O_2$ or by $FeTMPS/KHSO_5$ must be different.

Discussion

We found that FePcS associated with H_2O_2 can be useful in oxidation of polycyclic aromatic compounds. Anthracene was used as substrate to perform kinetic isotope studies and oxygen labeling experiments. Then we compared the results of the catalytic oxidations of anthracene by $FePcS/H_2O_2$ with those obtained with $FeTMPS/KHSO_5$ in order to gain a more complete view on the mechanisms of these oxidation reactions catalyzed by two related iron macrocyclic complexes. High-valent oxometal complexes have been proposed as active intermediates in hydrocarbon oxygenations (hydroxylations and epoxidations) using $KHSO_5$, NaOCl or *m*CPBA as oxidants and porphyriniron or -manganese compounds as catalysts[20][21][22]. We recently proposed a nucleophilic peroxoiron(III) complex of tetrasulfophthalocyanine, $PcSFe^{III}OOH$, as active species responsible for the oxidative cleavage of quinones generated during the oxidation of 2,4,6-trichlorophenol by $FePcS/H_2O_2$[15][16].

In the present work, several important differences must be noted in anthracene oxidations performed by $FePcS/H_2O_2$ or $FeTMPS/KHSO_5$. These differences are (i) a different composition of oxidation products depending on the oxidation system used (Scheme 2), (ii) a different reactivity of oxanthrone, which is relatively stable in the presence of $FeTMPS/KHSO_5$, but very quickly oxidized by $FePcS/H_2O_2$, (iii) and very different ^{18}O incorporations into anthrone and anthraquinone in experiments performed in the presence of $H_2{}^{18}O$ (Figure 3). On the other side, both catalytic systems, $FePcS/H_2O_2$ and $FeTMPS/KHSO_5$, showed essentially the same KIE values in the oxidation of anthracene (KIE = 0.75 and 0.76, respectively) or phenanthrene (KIE = 0.96 and 1.02, respectively) (Table 2).

Mechanistic Significance of Inverse Isotope Effects

The observation of a significant inverse isotope effect in the anthracene oxidation by $FePcS/H_2O_2$ or $FeTMPS/KHSO_5$ indicated that these KIEs could not be interpreted as primary KIEs involving a C−H(D) bond cleavage in the rate determining step of the initial step of the oxidation reaction. Consequently, these inverse KIEs precluded an oxygen rebound mechanism which involves a hydrogen atom abstraction from substrate by an electrophilic high-valent oxoiron complex to give a short-life radical intermediate followed by rapid recombination step[23]. Inverse KIEs are usually associated with secondary KIEs when no C−H(D) bond is cleaved or formed, but this bond should modify some parameters in the transition state (TS). This is usually the case when a C−H(D) bond is located at the reaction site itself, containing the leaving group (α secondary KIE) or at the adjacent carbon atom (β secondary KIE). In the case of the intermolecular $[H_{10}]$anthracene/$[D_{10}]$anthracene competitive oxidation an α secondary KIE is observed. Generally, the magnitude of an α-secondary KIE is determined by an inverse stretching and a normal bending contribution to the KIE value[24][25]. For example, in S_N2 reactions, a tighter TS, with short nucleophile α-carbon and/or α-carbon leaving group bond lengths, the KIE values would be inverse or normal and small[24]. Based on calculations with model systems, the α-secondary KIEs have been interpreted as reflecting the changes in the out-of-plane bending motion, i.e. hybridization changes or differences in the loose/tight character of the TS[26]. The activation energy for $sp^2 \rightarrow sp^3$ change in hybridization is lower for the deuterated substrate compared to the non-deuterated analogue, creating then an inverse KIE[27]. When the TS of the reaction occurs very late along the reaction coordinate, i.e. the TS exhibits essentially a fully sp^3-hybridized

carbon atom like in the reaction product, the k_H/k_D value will be more pronounced, the maximum KIE expected for a $sp^2 \rightarrow sp^3$ rehybridization will be 0.71[27]. Values of k_H/k_D ranging from 0.8 to 0.9 correspond to TS geometries somewhere between sp^2 and sp^3 and are more frequently observed. Inverse secondary KIEs have been measured for the addition of a variety of electrophilic reagents to olefins and aromatics, e.g. for the reaction of 1-naphthylcarbene to toluene ($k_H/k_D = 0.52$)[28]. An other example of an inverse α-secondary k_H/k_D equal to 0.83 has been recently observed during of the [2 + 2] photocycloaddition of arylalkenes to C_{60}[29]. Inverse KIEs have been reported for styrene epoxidations catalyzed by cytochrome P-450 ($k_H/k_D = 0.93$) or performed with *m*-chloroperbenzoic acid ($k_H/k_D = 0.82$)[27a] or by hexacyanoferrate(III) in acid medium ($k_H/k_D = 0.80$)[27b]. The cytochrome P-450 catalyzed oxidation of isotopically labeled chlorobenzenes provides also an inverse KIE (0.95)[30]. This result has been explained by an initial attack of an activated triplet-like oxygen atom on the π-system of substrate to generate a tetrahedral intermediate followed by rearrangement to phenol directly or via epoxide or ketone intermediates[30]. The aromatic hydroxylation of *o*- and *p*-xylene, catalyzed by cytochrome P-450, showed also an inverse α-secondary isotope effects (0.83−0.94) which were consistent with an addition reaction of a oxoiron species onto an sp^2-hybridized carbon atom[31]. The inverse nature of KIEs was anticipated for sp^2-to-sp^3 rehybridization during the covalent modification of human 5α-reductases by finasteride (a specific inhibitor) by a nucleophilic N addition to the double bond of this steroid-type molecule[32]. The reaction of the nitroethane anion (the α-carbon atom is sp^2-hybridized) with D-amino acid oxidase proceeds with an inverse $k_H/k_D = 0.84$ which was indicative of significant sp^2-to-sp^3 rehybridization in the TS[33]. Apart from the sp^2-to-sp^3 rehybridization, inverse isotope effects can be due to the difference in C−H and C−D distances, C−D bond being slightly shorter than corresponding C−H bond (d = 1.112 and 1.107 Å, respectively)[34]. The racemization of 2,2′-dibromo-4,4′-dicarboxybiphenyl[35] and 9,10-dihydro-4,5-dimethylphenanthrene[36] showed inverse KIEs of 0.85 and 0.88, respectively. The origin of a large inverse secondary KIE in the bromination of a sterically congested olefin (0.36−0.65) has been attributed to the fact that C−D bonds are shorter and less sterically demanding[37]. Large inverse equilibrium isotope effects have also been observed for the oxidative addition of H_2 to *trans*-$W(PMe_3)_4I_2$ ($K^H_{eq}/K^D_{eq} = 0.63$)[38a] and cyclohexane to $CpRh(CO)_2$ ($K^H_{eq}/K^D_{eq} = 0.1$, at 163−193 K)[38b]. Recently, a substantial inverse isotope effect of $k_H/k_D = 0.48$ has also been published in Co^{III}-catalyzed polymerization of ethylene[39] and explained by the presence of a β-agostic Co···H···C (Co···D···C) interaction, the inverse KIE being associated with the release of the agostic bond. Related to this interpretation of an inverse KIE, it must be noted that complexation of *n*-heptane with double A-frame porphyriniron(III) has been recently observed in crystals[40]. An out-of-plane displacement of the iron center of 0.26 Å and an Fe···C distance of 2.5 Å strongly suggest moderate to weak agostic interactions between C−H bonds of the alkane and the metal center. *p*-Xylene can interact with the metal center of an porphyriniron(III), the smallest Fe−C distance was 2.94 Å and the iron atom was drawn 0.07 Å out of the mean plane of the porphyrin core indicating a possible weak agostic interaction[41].

In the present case of the oxidation of anthracene catalyzed by phthalocyanine- or porphyriniron complexes, anthracene, a polyaromatic substrate, should have a pronounced tendency to form a stacking complex with FePcS or FeTMPS. A rather polar reaction medium (an acetonitrile/water mixture) should favor stacking interactions between two large planar hydrophobic molecules. Then a question arises: can the difference in C−H/C−D substitution on anthracene generate different stacking interactions between $[H_{10}]$anthracene or $[D_{10}]$anthracene with the macrocyclic plane molecule of FePcS or FeTMPS? In other words, are the observed KIEs only related to hydrophobic interactions between the aromatic substrate and the macrocyclic catalyst? The differences observed on inverse KIEs during the $[H_{10}]$anthracene/$[D_{10}]$anthracene and $[H_{10}]$anthracene/$[D_2]$anthracene competitive oxidations (Table 2) could be due to possible differences in stacking interactions between $[D_{10}]$anthracene and $[D_2]$anthracene with the macrocycle of the catalyst resulting from a slight difference of the nature of C−H bonds compared to C−D bonds. So, the stacking interactions should increased with the deuterium content of anthracene. This is the case with both catalytic systems: the KIE is 0.90 for $[D_2]$anthracene and 0.75 with $[D_{10}]$anthracene with $FePcS/H_2O_2$ (0.95 and 0.76 with $FeTMPS/KHSO_5$, respectively) (Table 2). Consequently, the value of the inverse KIE due to the sp^2-to-sp^3 hybridization change should be enhanced in a highly stacked substrate-catalyst intermediate during the addition of an electrophilic oxoiron complex to the sp^2-carbon atom of anthracene to give a σ adduct. The data on ^{18}O labeling experiments are also consistent with this proposal (see below).

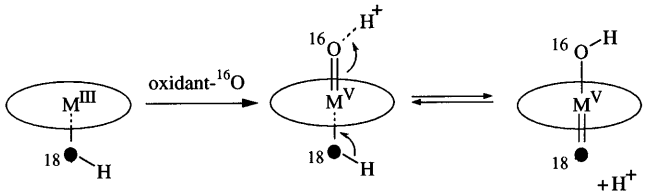
The quasi-absence of KIE observed in the phenanthrene oxidation by $FePcS/H_2O_2$ or by $FeTMPS/KHSO_5$ (0.96 and 1.02, respectively) can be due to the reduction of stacking interactions compared to anthracene and also to the different nature of C9−H and C10−H bonds in phenanthrene. The C9−C10 bond of phenanthrene exhibits a relatively high bond order, indicating that it possesses a considerable degree of double bond character (K region bonds of polyaromatics), while anthracene bonds show essentially an aromatic character (*meso* region bonds)[42]. As a result, the main product of phenanthrene oxidation was biphenyl-2,2′-dicarboxylic acid. A similar cleavage of the double bond of styrene was observed when oxidized by $FePcS/H_2O_2$[16].

Mechanistic Significance of ^{18}O Labeling Experiments

In aqueous media oxo(porphyrin)metal(V) complexes have an axial hydroxo ligand. In order to explain the observed 50% ^{18}O incorporation from $H_2{}^{18}O$ in epoxides during olefin epoxidations by a metalloporphyrin/$KHSO_5$ system[20a][21b][21c], hydroxylation of DNA deoxyriboses[20b] or

C−H bond hydroxylation of 4-isopropylbenzoic acid[20c] it was proposed that the active hydroxo(oxo)(porphyrin)metal(V) complex undergoes a "redox tautomerism" (Figure 4). The ^{18}O incorporation depends on the reaction conditions[21b], primarily on relative kinetics of oxidation step and ligand exchange processes between the hydroxo ligand and bulk water and the nature of the catalyst. The rate of the oxo-hydroxo interchange in the oxo(porphyrin)manganese(V) complex was estimated to be about 10^3 s^{-1}[21c].

Figure 4. Redox tautomerism in a hydroxo(oxo)metal(V) species having a water-soluble porphyrin ligand (O = ^{16}O, black O = ^{18}O)



The large ^{18}O incorporation into anthrone (63%) and anthraquinone (55%) observed during FeTMPS/KHS$^{16}O_5$ anthracene oxidation in the presence of $H_2{}^{18}O$ is consistent with the involvement of oxo(porphyrin)iron complex as active species. By contrast, the absence of ^{18}O incorporation into anthrone, produced in the oxidation by FePcS/H_2O_2, could be explained by the involvement of an active oxo-metal species unable to undergo such an oxo-hydroxo equilibrium (in particular if there is no hydroxo ligand in the axial position *trans* to the oxo group).

Tautomeric Equilibria in Oxidation Products of Anthracene

The sequence of anthracene oxidation to anthraquinone and the relation between tautomeric forms of products are depicted in Scheme 5. The first oxidation product, 9-hydroxyanthracene is in fast keto-enol equilibrium with anthrone, which is the predominant form. The anthrone/9-hydroxyanthracene ratio determined by NMR in $CDCl_3$ at 25°C was estimated to be 80:20[43]. 9,10-Dihydroxyanthracene exists in solution in equilibrium with oxanthrone (K_{eq} = 0.13) and is the major tautomer (89%)[44]. However, the equilibrium is reached very slowly. The rate constants for the 9,10-dihydroxyanthracene-oxanthrone interconversion were determined to be $k_{-2} = 3 \times 10^{-6}$ s^{-1} and $k_2 = 4 \times 10^{-7}$ s^{-1}[45]. It means that in 1 mM solution only 1% of oxanthrone will be transformed into 9,10-dihydroxyanthracene after 1 h at room temperature.

Mechanism of Anthracene Oxidation by FeTMPS/$KHSO_5$

The oxidation of anthracene by FeTMPS/$KHSO_5$ was significantly faster than those of anthrone and oxanthrone. Under the same conditions the conversions of anthracene, anthrone and oxanthrone after 30 min were 100, 38 and 18%, respectively. These data indicated that there was an oxidation pathway to give directly oxanthrone, the main oxidation product, without intermediate formation of anthrone.

An electrophilic attack of a high-valent oxo(porphyrin)-iron complex at a central sp^2-carbon atom of anthracene to give a σ complex is probably the initial oxidation step (Figure 5). The inverse isotope effect, indicative of an sp^2-to-sp^3 rehybridization in the TS containing both substrate and catalyst stacked and the observed ^{18}O incorporation into anthrone, the first oxidation product, typical for oxoiron complex mediated oxidation in aqueous medium strongly suggested the formation of a new carbon−oxygen bond to form a σ complex **A**. This intermediate **A** can be trapped by O_2 to produce oxanthrone and anthraquinone via an intermediate radical **B**. An intramolecular electron transfer in intermediate **A** can lead to an intermediate carbocation **C**, which can undergo either a proton elimination to give a σ complex **D** or a nucleophilic attack of water to produce an intermediate **E**, providing a reaction pathway for oxanthrone formation without intermediate formation of anthrone. The hydrolysis of the Fe^{III}−O−aromatic bond in both intermediates **D** and **E** gave 9-hydroxyanthracene (quickly tautomerized to anthrone) and 9,10-dihydro-9,10-dihydroxyanthracene **F**. Then **F** can be further oxidized by a $2e^-$ process with the release of $2H^+$, producing oxanthrone with an increased ^{18}O content, or by oxidation of a C−H bond by an oxygen rebound mechanism. The GC-MS analysis of [H_{10}]anthracene/[D_{10}]anthracene oxidation products after 6 min of reaction revealed that anthraquinone was enriched with nondeuterated material: 57% of [H_8]anthraquinone and 43% of [D_8]anthraquinone, indicating a KIE value > 1 on the anthrone-to-anthraquinone oxidation step. The ^{18}O content in anthraquinone (55%) was not increased compared to that in anthrone (63%). Both findings suggest that oxidation of intermediate **F** proceeds by an oxygen rebound mechanism followed by H_2O elimination to generate oxanthrone. The fact that the metallopor-

Scheme 5. Oxidation products of anthracene and tautomeric equilibria for anthrone and oxanthrone

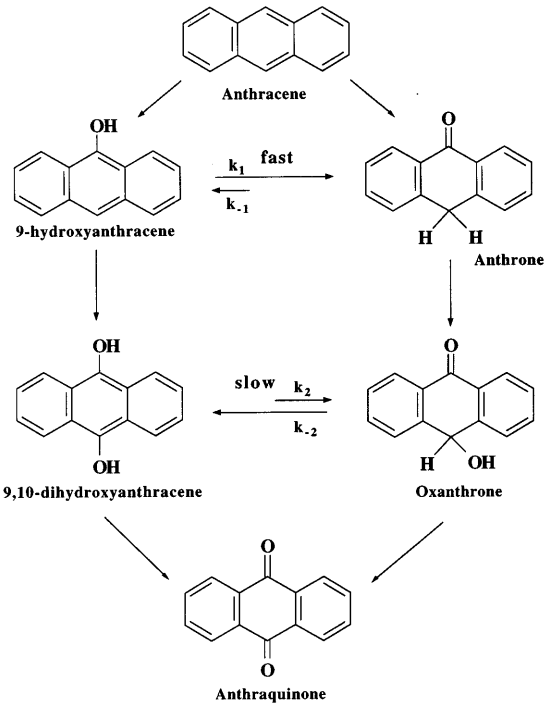
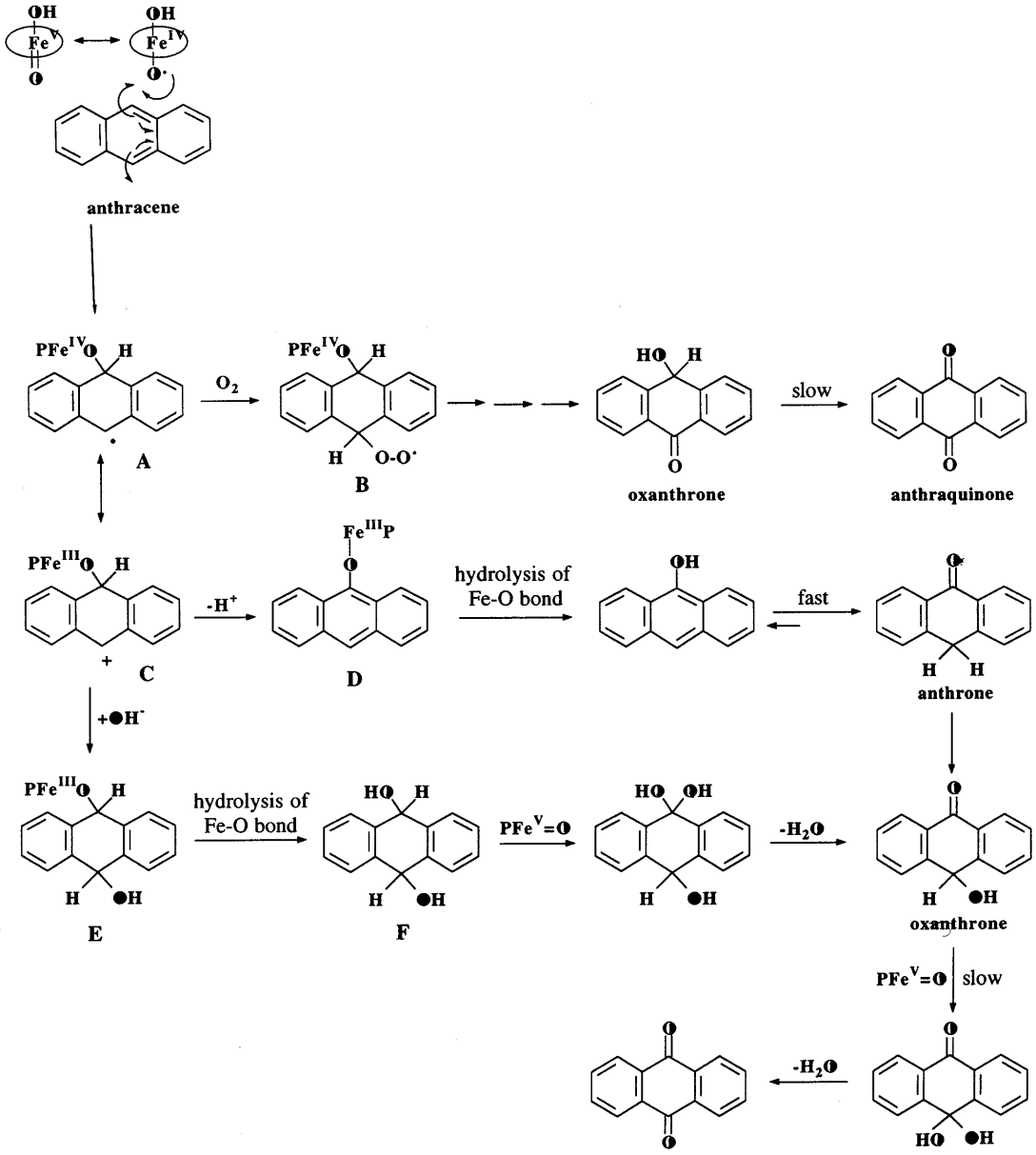


Figure 5. Proposed mechanism for anthracene oxidation by FeTMPS/$KHSO_5$ (O = ^{16}O, black ● = ^{18}O)

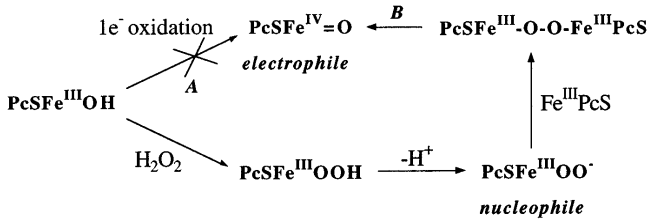


phyrin-catalyzed oxidation of anthracene gave oxanthrone, not the more oxidizable 9,10-hydroxyanthracene tautomeric form, explains the rather low yield of anthraquinone, since oxanthrone is relatively stable under the reaction conditions (oxanthrone conversion being only 23% after 60 min).

Active Species in FePcS/H_2O_2 Oxidations

In the FePcS/H_2O_2 mediated oxidation of trichlorophenol[15][17] a nucleophilic $PcSFe^{III}OO^-$ complex was proposed to be the active species, able to perform two key steps: (i) a nucleophilic addition to the electron-deficient double bond of intermediate quinones to provide epoxy quinones and (ii) a nucleophilic attack on the carbonyl group of the different quinones, leading to their ring cleavage[16]. Although the addition of nucleophiles to polyarenes, e.g. the addition of alkyllithium reagents to anthracene, has been published[46], such a peroxoiron(III) complex is probably not nucleophilic enough for a direct attack onto an sp^2-carbon atom of a PAH. Another possible active metal-oxygen species could be a high-valent oxoiron complex, having two redox equivalents above the Fe^{III} state. Several lines of evidence indicate that it is not the case for the FePcS/H_2O_2 system[15b]. The fact that the oxygen atom in anthrone originated from H_2O_2 (Figure 3) also indicated that an oxoiron(V) complex was not involved in anthracene oxidation by FePcS/H_2O_2. With such an oxoiron(V) complex we could expect both ^{16}O and ^{18}O incorporations due to redox tautomerism, as observed in anthracene oxidation by FeTMPS/$KHSO_5$. The other possible formulation of the active species involved in PAH oxidations by FePcS/H_2O_2 is a $PcSFe^{IV}=O$ species[15b]. It can be formed by a $1e^-$ oxi-

Figure 6. Generation of peroxoiron(III) and oxoiron(IV) species by activation of FePcS with hydrogen peroxide

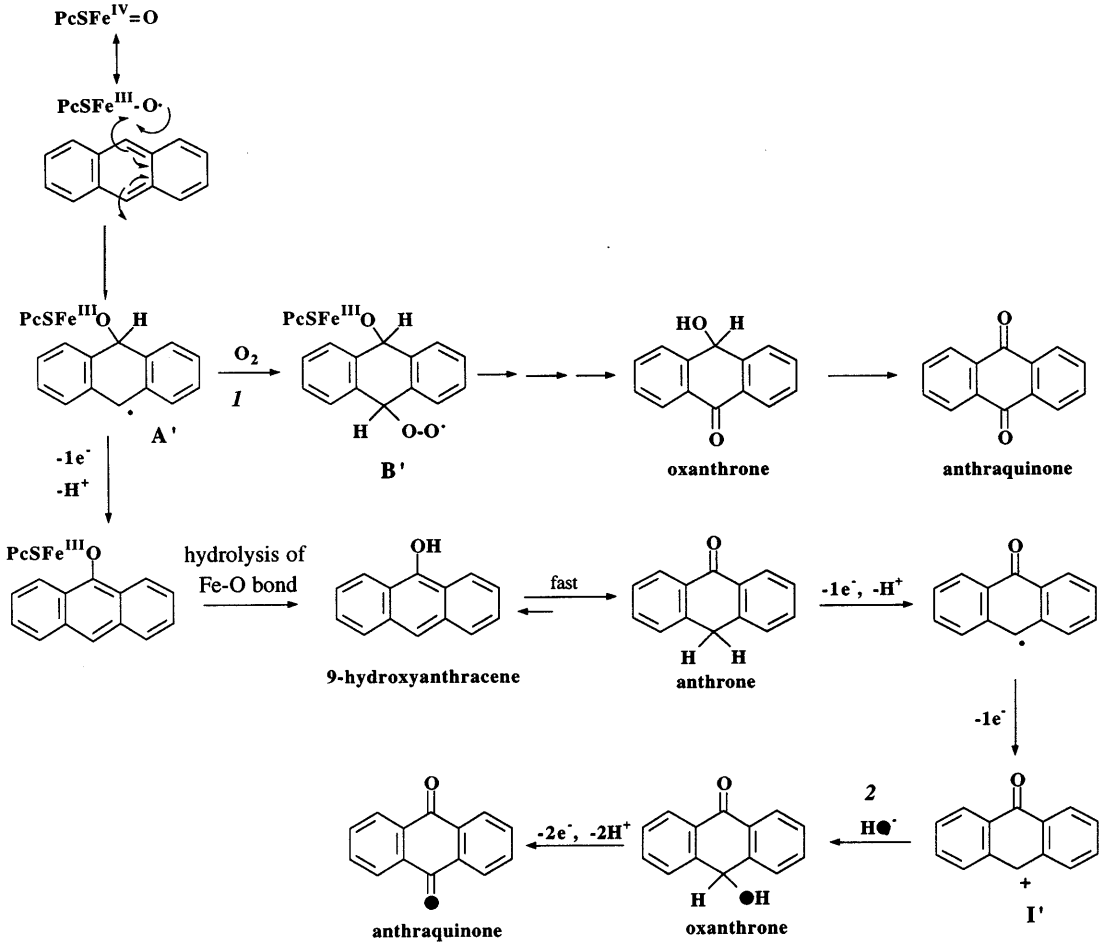


dation of $PcSFe^{III}OH$ complex (Figure 6, pathway *A*) or by the intermediate formation of a μ-peroxo dimer (pathway *B*). In the former case ^{18}O from water should be found in anthrone obtained in the presence of $H2^{18}O$. The absence of ^{18}O incorporation into anthrone during the oxidation of anthracene by $FePcS/H_2O_2$ in $H_2{}^{18}O$ eliminated this possibility. Consequently, $PcSFe^{IV}=O$ should be formed by pathway *B* by the homolytic cleavage of a μ-peroxo dimer (we proposed the pathway *A* in ref.[15b] before having on hands the data of these labeling studies). This $PcSFe^{IV}=O$ species is neutral and does not require the presence of an anionic axial anion ligand (e.g. HO^-) to compensate a charge. Consequently, no redox tautomerism is possible in the absence of HO^- ligand *trans* to the oxo entity. This absence of redox tautomerism for $PcSFe^{IV}=O$ explained the 100% incorporation of ^{16}O into anthrone during the $FePcS/H_2O_2$ oxidation of anthracene performed in heavy water.

Mechanism of Anthracene Oxidation by $FePcS/H_2O_2$

The first step of the $FePcS/H_2O_2$ mediated oxidation of anthracene resembles that described in the FeTMPS/$KHSO_5$ oxidation (Figure 7). The nearly identical inverse KIE (0.75) found for the first reaction step suggested also the formation of a σ complex, intermediate **A′** which can be trapped by O_2 to produce oxanthrone and anthraquinone via a radical intermediate **B′**. The significant ^{16}O incorporation in anthraquinone when the oxidation was performed under air compared to that obtained under nitrogen (Figure 3) was strongly indicative of this pathway 1. Hydrolysis of the $Fe^{III}-O-$aromatic bond followed by proton elimination and $1e^-$ oxidation generated 9-hydroxyanthracene which rapidly tautomerized to the thermodynamically favored anthrone. Successive $1e^-$ oxidation and proton elimination steps gives rise to carbocation **I′**, which can react with water (pathway 2) to produce oxanthrone and anthraquinone. $PcSFe^{IV}=O$ complex is not such a strong oxidant to perform the abstraction of an H atom of a aliphatic or aromatic C−H bond. However, $PcSFe^{IV}=O$ is

Figure 7. Proposed mechanism for anthracene oxidation by $FePcS/H_2O_2$ (O = ^{16}O, black ● = ^{18}O)



probably a sufficiently good $1e^-$ oxidant to perform $1e^-$ oxidations of intermediate products or of oxanthrone by successive $1e^-$ oxidations and proton eliminations to provide anthraquinone.

The rather low yields of anthrone and anthraquinone after 30 min (5 and 21%, respectively) might be due to radical intermediates capable of undergoing side reactions, e.g. coupling reactions. Accordingly, the presently proposed mechanism, the first oxygen atom incorporated into the different products originates from $PcSFe^{IV}=O$ (^{16}O in labeling experiments), and the value of ^{18}O incorporation of the second oxygen atom of anthraquinone from $H_2{}^{18}O$ will depend on the relative rates of the different pathways indicated on Figure 7. Very significant ^{18}O incorporation into the second oxygen position of anthraquinone under air (64%) and, especially under nitrogen (88%), strongly suggest that pathway 2 is the major reaction pathway.

Conclusion

The (tetrasulfophthalocyanine)iron/hydrogen peroxide oxidation system, based on an easy-to-prepare catalyst and a "clean" oxidant, is capable of oxidizing polycyclic aromatic hydrocarbons, like anthracene, phenanthrene and benzo[*a*]pyrene. Data obtained from product distribution, kinetic isotope effects and ^{18}O labeling studies, as well as a comparative study of anthracene oxidation by FeTMPS/$KHSO_5$ allowed us to propose that an oxo(phthalocyanine)iron(IV) complex, is probably responsible of these PAH oxidations. Consequently, taking in consideration the previously reported mechanistic studies on quinone cleavage by the same $FePcS/H_2O_2$ system, two kinds of the active species can be generated from FePcS in the presence of H_2O_2: (i) a nucleophilic peroxoiron complex $PcSFe^{III}OO^-$ responsible for double carbon−carbon bond cleavage in the deep oxidation of trichlorophenol[15][16] and (ii) an electrophilic $PcSFe^{IV}=O$ complex capable of oxidizing aromatic hydrocarbons by the formation of a σ adduct. This versatility makes (tetrasulfophthalocyanine)iron in association with hydrogen peroxide a suitable catalytic method for the chemical degradation of different pollutants.

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Experimental Section

Instrumentation: Gas chromatography-mass spectrometry (GC-MS) was performed with a Hewlett-Packard 5890 instrument using electron-impact ionization at 70 eV. The carrier gas for GC-MS was He, and a 12 m × 0.2 mm HL-1 (Crosslinked Methyl Silicone Gum) capillary column was used. − High performance liquid chromatography (HPLC) analyses were performed with a Waters-486 Liquid Chromatograph equipped with a μ-Bondapak C18 column, eluent being a mixture of methanol and water (85:15, v/v) at a flow rate of 1 ml min^{-1}, detection at 242 nm for anthracene, 252 nm for phenanthrene and 280 nm for benzo[*a*]pyrene analyses. − UV/Vis spectra were recorded with a Hewlett-Packard 8452A diode array spectrophotometer. − ^1H NMR spectra were recorded with Bruker WM 250 spectrometer.

Materials: All chemicals used were of reagent grade. Potassium monopersulfate was a gift from Interox (Curox^R) and is the triple salt $2KHSO_5{\cdot}KHSO_4{\cdot}K_2SO_4$. Hydrogen peroxide was obtained from Janssen Chimica as a 35% aqueous solution. $H_2{}^{18}O$ (98 atom-%) was supplied by Eurisotop (Gif-sur-Yvette, France). Lithium aluminum deuteride was purchased from Fluka (minimum 99 atom-% D). (Tetrasulfophthalocyanine)iron (FePcS) was prepared according to the method of Weber and Busch.[47] The iron complex of octasodium *meso*-tetrakis(3,5-disulfonatomesityl)porphyrin (TMPS) was synthesized according to ref.[48]. Anthracene (97%), phenanthrene (98%), benzo[*a*]pyrene (98%), [D_{10}]anthracene (> 98 atom-% D), [D_{10}]phenanthrene (97 atom-% D), anthrone (96%), anthraquinone (97%), phenanthrenequinone (99%), 9,10-dibromoanthracene (98%) were purchased from Aldrich. Oxanthrone was prepared from anthrone via 10-bromoanthrone according to ref.[45]. NMR (CD_2Cl_2): δ = 2.47 (d, 1 H, *J* = 9.5 Hz, OH), 5.78 (d, 1 H, *J* = 9.5 Hz, H_{10}), 7.54 (td, 2 H, *J* = 7.5 and 0.7 Hz, H_3), 7.73 (td, 2 H, *J* = 7.5 and 1.5 Hz, H_2), 7.90 (dd, 2 H, *J* = 7.5 and 0.7 Hz, H_4), 8.25 (dd, 2 H, *J* = 7.5 and 1.5 Hz, H_1); (CD_2Cl_2 + small amount of D_2O): the same signals, except doublet at δ = 2.47 disappeared and the doublet at δ = 5.78 became a singlet.

Preparation of 9,10-Dideuterioanthracene: The procedure was adapted from ref.[49]. Dibromoanthracene (1.008 g, 3 mmol) and $LiAlD_4$ (504 mg, 12 mmol) were added under nitrogen to 15 ml of anhydrous dimethoxyethane. The reaction mixture, contained in a 50-ml round-bottom single-neck flask and maintained under nitrogen, was partly submerged in a ultrasonic laboratory cleaner Branson 2200 (working frequency 47 kHz, 205 W) at 35−40°C. The reaction was monitored by GC-MS. After 13 h, all dibromoanthracene was reduced and the reaction mixture contained 9,10-dideuterioanthracene accompanied by minor amount of 9-bromo[D_1]-anthracene.The reaction mixture was cooled at −40°C and 1 ml of D_2O (99%) was slowly added. The temperature was allowed to return to 20°C and hydrolysis of the excess of $LiAlD_4$ was performed for 30 min. Then the resulting mixture was pourred into 30 ml of water and extracted with diethyl ether (4 × 40 ml). The combined organic extracts were washed with saturated NaCl solution, dried with Na_2SO_4 and concentrated. The white precipitate was separated by filtration and recrystallized from diethyl ether to give 148 mg (27% yield) of the pure 9,10-dideuterioanthracene material. The isotopic purity was determined by NMR and GC-MS methods. The material contained 72.8% of 9,10-dideuterioanthracene and 27.2% of 9-deuterioanthracene.

General Catalytic Procedure for PAH Oxidation: Oxidation of anthracene was carried out in a mixture of acetonitrile/50 mM phosphate buffer at pH = 7 (3:1, v/v) at 20°C under aerobic conditions. Oxidations of phenanthrene and benzo[*a*]pyrene were performed in acetonitrile/33.3 mM phosphate buffer at pH = 4.6 (1:1, v/v). The reaction mixture (2 ml) contained 2 μmol of substrate introduced as a 4 mM acetonitrile solution and 0.074 or 0.1 μmol of catalyst, introduced as a 1.28 mM solution in water, and the required amounts of acetonitrile and stock buffer solution to obtaine the desired organic solvent/water ratios. Oxidations were started by addition of 10 μmol of oxidant (10 μl of 3.5% H_2O_2 solution or 3.1 mg of potassium monopersulfate). The final concentrations of the catalyst, substrate and oxidant were 37 (or 100) μM, 1 mM and 5 mM, respectively. The reactions were followed by HPLC and GC-MS techniques. Anthraquinone and anthrone were identified by comparison of its GC-MS behavior (retention time and mass spectrum) with those of an authentic sample. Oxanthrone was identified by comparison of its NMR spectrum with that of an authentic sample.

$H_2{}^{18}O$ Experiments: Reactions were carried out using $H_2{}^{18}O$ (98 atom-%) according to the following procedure. A mixture of 25 μl of 0.5 M phosphate buffer pH = 7 and 29 μl of catalyst stock solution (1.28 mM in water) was dried under vacuum. The dry residue was then dissolved in 250 μl of $H_2{}^{18}O$ and 250 μl of [H_{10}]anthracene and [D_{10}]anthracene stock solutions (50:50 mixture, 4 mM total concentration in MeCN) and 500 μl of MeCN were added. The oxidations were performed under air and under nitrogen. In the latter case the reaction mixture was submitted to 3 freeze-pump-thaw cycles and the reaction flask was filled up with nitrogen. The reaction was started by the addition of 5 μl of 3.5% H_2O_2 (for FePcS oxidation) or 1.6 mg of $KHSO_5$ (for FeTMPS oxidation). The substrate conversion was monitored by HPLC and isotopic compositions of products were analyzed by GC-MS.

Determination of Isotopic Composition of Substrates and Products: Mass spectra of [H_{10}]anthracene and [D_{10}]anthracene show very strong molecular peaks accompanied with little fragmentations. [H_{10}]anthracene: MS; *m/z* (%): 178 (100) [M^+], 176 (18) [M − 2 H]$^+$, 152 (8) [M − C_2H_2]$^+$, 89 (13) [M − C_7H_5]$^+$. [D_{10}]anthracene: MS; *m/z* (%): 188 (100) [M^+], 184 (13) [M − 2 D]$^+$, 160 (9) [M − C_2D_2]$^+$, 94 (17) [M − C_7D_5]$^+$. So, under conditions of GC-MS analysis, within experimental error, there is no isotope effect on fragmentation and isotopic compositions of [H_{10}]anthracene and [D_{10}]anthracene can be determined from the intensities of corresponding molecular peaks. The mass spectra of phenanthrene and products of oxidation of anthracene and phenanthrene showed the same features and their isotopic compositions were determined from the intensities of the molecular peaks of deuterated and non-deuterated compounds.

KIE determinations based on [H_{10}]anthracene/9,10-dideuterioanthracene oxidations were performed taking into account admixture of monodeuterated anthracene, the presence of [M + 1] peaks due to ^{13}C natural content and [M − 1] and [M − 2] fragmentations according to the following formalism:

$$I_{178} = [D_0]\text{-A} + F_{M-1}\cdot[D_1]\text{-A} + F_{M-2}\cdot[D_2]\text{-A} \quad (2)$$

$$I_{179} = [D_1]\text{-A} + F_{M+1}\cdot[D_0]\text{-A} + F_{M-1}\cdot[D_2]\text{-A} \quad (3)$$

$$I_{180} = [D_2]\text{-A} + F_{M+1}\cdot[D_1]\text{-A} \quad (4)$$

where I_{178}, I_{179}, I_{180} were intensities of peaks at *m/z* 178, 179 and 180, respectively; [D_0]-A, [D_1]-A, [D_2]-A were percentages of corresponding isotopomers of anthracene; F_{M+1}, F_{M-1}, F_{M-2} were relative intensities of [M + 1], [M − 1] and [M − 2] peaks. The latter intensities were determined in separate GC-MS experiments to be $F_{M+1\,=\,0}$.15, F_{M-1} = 0.11, F_{M-2} = 0.18. KIEs were calculated from the data obtained on conversions and the percentages of [H_{10}]anthracene and 9,10-dideuterioanthracene in an initial reaction mixture and after several minutes when the substrate conversion was near 50%.

[1] C. E. Cerniglia, *Biodegradation* **1992**, *3*, 351−368.
[2] K. E. Hammel in *Degradation of Environmental Pollutants by Microorganisms and their Metalloenzymes. Metal Ions in Biological Systems* (Eds.: H. Sigel, A. Sigel), Marcel Dekker, New York, **1992**, vol. 28, p. 41.
[3] S. D. Haemmerli, M. S. A. Leisola, D. Sanglard, A. Fiechter, *J. Biol. Chem.* **1986**, *261*, 6900−6903.
[4] K. E. Hammel, B. Kalyanaraman, T. K. Kirk, *J. Biol. Chem.* **1986**, *261*, 16948−16952.
[5] J. D. Lipscomb, A. M. Orville in *Degradation of Environmental Pollutants by Microorganisms and their Metalloenzymes. Metal Ions in Biological Systems* (Eds.: H. Sigel, A. Sigel), Marcel Dekker, New York, **1992**, vol. 28, p. 243.
[6] D. A. Lane in *Chemical Analysis of Polycyclic Aromatic Compounds* (Ed.: T. Vo-Dinh), Wiley, New York, **1989**, p. 31.
[7] For a review on chemistry of polyarenes see: R. G. Harvey, *Polycyclic Aromatic Compounds*, Wiley, New York, **1997**, p. 96.
[8] M. Juaristi, J. M. Aizpurua, B. Lecea, C. Palomo, *Can. J. Chem.* **1984**, *62*, 2941−2944.
[9] E. V. Dehmlov, J. K. Makrandi, *J. Chem. Research (S)* **1986**, 32−33.
[10] D. Villemin, M. Ricard, *Nouv. J. Chem.* **1984**, *8*, 185−189.
[11] W. Adam, P. A.Ganeshpure, *Synthesis* **1993**, 280−282.
[12] [12a] R. Song, A. Sorokin, J. Bernadou, B. Meunier, *J. Org. Chem.* **1997**, *62*, 673−678. − [12b] G. J. Harden, M. M. Coombs, *J. Chem. Soc., Perkin Trans. 1* **1995**, 3037−3042.
[13] T. Higuchi, C. Satake, M. Hirobe, *J. Am. Chem. Soc.* **1995**, *117*, 8879−8880.
[14] S. V. Barkanova, V. M. Derkacheva, O. V. Dolotova, V. D. Li, V. M. Negrimovsky, O. L. Kaliya, E. A. Luk′yanets, *Tetrahedron Lett.* **1996**, *37*, 1637−1640.
[15] [15a] A. Sorokin, J.-L. Séris, B. Meunier, *Science* **1995**, *268*, 1163−1166. − [15b] B. Meunier, A. Sorokin, *Acc. Chem. Soc.* **1997**, *30*, 470−476.
[16] [16a] A. Sorokin, B. Meunier, *Chem. Eur. J.* **1996**, *2*, 1308−1317. − [16b] A. Sorokin, S. De Suzzoni-Dezard, D. Poullain, J.-P. Noël, B. Meunier, *J. Am. Chem. Soc.* **1996**, *118*, 7410−7411. − [16c] A. Hadasch, A. Sorokin, A. Rabion, B. Meunier, *New J. Chem.* **1998**, 45−51.
[17] A. Sorokin, L. Fraisse, A. Rabion, B. Meunier, *J. Mol. Cat.* **1997**, *117,* 103−114.
[18] R. J. Lorentzen, J. Caspary, S. A. Lesko, P. O. Ts′o, *Biochemistry* **1975**, *14*, 3970−3977.
[19] L. Melander, J. M. Saunders, *Reaction Rates of Isotopic Molecules*, Wiley, New York, **1980**, p. 95.
[20] [20a] J. Bernadou, A.-S. Fabiano, A. Robert, B. Meunier, *J. Am. Chem. Soc*. **1994**, *116*, 9375−9376. − [20b] M. Pitié, J. Bernadou, B. Meunier, *J. Am. Chem. Soc*. **1995**, *117*, 2935−2936. − [20c] R. J. Balahura, A. Sorokin, J. Bernadou, B. Meunier, *Inorg. Chem.* **1997**, *36*, 3488−3492.
[21] [21a] W. Nam, J. S. Valentine, *J. Am. Chem. Soc*. **1993**, *115*, 1772−1778. − [21b] K. A. Lee, W. Nam, *J. Am. Chem. Soc*. **1997**, *119*, 1916−1922. − [21c] J. T. Groves, J. Lee, S. S. Marla, *J. Am. Chem. Soc*. **1997**, *119*, 6269−6273.
[22] B. Meunier, *Chem. Rev.* **1992**, *92*, 1411−1456.
[23] [23a] T. J. McMurry, J. T. Groves, In *Cytochrome P-450 Structure, Mechanism and Biochemistry* (Ed.: P. R. Ortiz de Montellano), Plenum, New York, **1986**; pp. 1−28. − [23b] M. Newcomb, M.-H. Le Tadic-Biadatti, D. L. Chestney, E. S. Roberts, P. F. Hollenberg, *J. Am. Chem. Soc*. **1995**, *117*, 12085−12091.
[24] R. A. Poirier, Y. Wang, K. C.Westaway, *J. Am. Chem. Soc.* **1994**, *116*, 2526−2533.
[25] S. Wolfe, C.-K. Kim, *J. Am. Chem. Soc.* **1991**, *113*, 8056−8061.
[26] [26a] P. A. Nielsen; S. S. Glad, F. Jensen, *J. Am. Chem. Soc.* **1996**, *118*, 10577−10583. − [26b] S. S. Glad, F. Jensen, *J. Am. Chem. Soc.* **1997**, *119*, 227−232.
[27] [27a] R. P. Hanzlik, G. O. Shearer, *Biochem. Pharm.* **1978**, *27*, 1441−1444 and references therein. − [27b] A. K. Bhattacharjee, M. K. Mahanti, *Gazz. Chim. Ital.* **1984**, *114*, 337−340.
[28] G. W. Griffin, K. A. Horn, *J. Am. Chem. Soc.* **1987**, *109*, 4919−4926 and references therein.
[29] G. Vassilikogiannakis, M. Orfanopoulos, *J. Am. Chem. Soc.* **1997**, *119*, 7394−7395.
[30] K. R. Korzekwa, D. C. Swinney, W. F. Trager, *Biochemistry* **1989**, *28*, 9019−9027.
[31] R. P. Hanzlik, K.-H. J. Ling, *J. Am. Chem. Soc.* **1993**, *115*, 9363−9370.
[32] G. Tian, S.-Y. Chen, K. L. Facchine, S. R. Prakash, *J. Am. Chem. Soc.* **1995**, *117*, 2369−2370.
[33] K. A. Kurtz, P. F. Fitzpatrick, *J. Am. Chem. Soc.* **1997**, *119*, 1155−1156.
[34] J. March, *Advanced Organic Chemistry: Reactions, Mechanisms and Structure*, 4th ed., Wiley, New York, **1992**, p. 20.
[35] L. Melander, R. E. Carter, *Acta Chem. Scand*. **1964**, *18*, 1138−1149.
[36] K. Mislow, R. Graeve, A. J. Gordon, G. H. Wahl, Jr., *J. Am. Chem. Soc.* **1963**, *85*, 1199−1200.
[37] R. W. Nagorski, H. Slebocka-Tilk, R. S. Brown, *J. Am. Chem. Soc.* **1994**, *116*, 419−420.
[38] [38a] D. Rabinovich, G. Parkin, *J. Am. Chem. Soc.* **1993**, *115*, 353−354. − [38b] R. H. Schultz, A. A. Bengali, M. J. Tauber, B. H. Weiller, E. P. Wasserman, K. R. Kyle, C. B. Moore, R. G. Bergman, *J. Am. Chem. Soc.* **1994**, *116*, 7369−7377.
[39] M. J. Tanner, M. Brookhart, J. M. DeSimone, *J. Am. Chem. Soc.* **1997**, *119*, 7617−7618.

[40] D. R. Evans, T. Drovetskaya, R. Bau, C. A. Reed, P. D. W. Boyd, *J. Am. Chem. Soc.* **1997**, *119*, 3633−3634.
[41] Z. Xie, R. Bau, C. A. Reed, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2433−2434.
[42] See ref.[7], p. 26.
[43] T. R. Criswell, B. H. Klanderman, *J. Org. Chem.* **1974**, *39*, 770−774.
[44] K. Brederesk, E. F. Sommermann, *Tetrahedron Lett.* **1966**, *41*, 5009−5014.
[45] S. A. Carlson, D. H. Hercules, *Anal. Chem.* **1973**, *45*, 1794−1799.
[46] P. P. Fu, R. G. Harvey, *Chem. Rev.* **1978**, *78*, 317−361.
[47] J. H. Weber, D. H. Busch, *Inorg. Chem.* **1965**, *4*, 469−471.
[48] P. Hoffmann, G. Labat, A. Robert, B. Meunier, *Tetrahedron Lett.* **1990**, *31*, 1991−1994.
[49] B. H. Han, P. Boudjouk, *Tetrahedron Lett.* **1982**, *23*, 1643−1646.

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