The oxidation of styrene in the presence of thiols and iron porphyrin

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Abstract

Benzaldehyde and a methyl sulfide, formed from the thiol used, are two major products of the title reaction in methoxyethanol. Primary alkyl thiols were less active than secondary ones, but the most active system was obtained with an aryl thiol, benzenethiol. Therefore, detailed studies were carried out with it. The reaction towards benzaldehyde and the methyl sulfide proceeded only in the presence of iron porphyrins. When the catalyst degraded, only side reactions, disulfide formation and anti-Markovnikov addition occurred. Thiols do not act as sacrificial reductants in the studied system. UV-Vis spectra revealed the formation of an iron(III) porphyrin radical cation. It was present only in the active phase of the reaction. Since it was formed with some delay, it did not make an intermediate of the studied reaction but seemed to be in equilibrium with it.

1. Introduction

Thiols are so readily oxidised that under oxidation reaction conditions could be thought to act as sacrificial reductants, unless bound in a manner inhibiting their oxidation. On the other hand, they modify the iron porphyrin centre so advantageously for oxidation reactions [1,2] that their use is very tempting. There is a danger though that thiols would promote the degradation of the porphyrin ring [3], which is the case in plant peroxidases that degrade protoporphyrin IX in the presence of thiol containing substrates, such as glutathione and cysteine [4].

Most studies on metalloporphyrin catalytic systems are devoted to models of cytochrome P-450, haem-containing monooxygenases [5]. They use only one oxygen atom out of two from the O_2 molecule and require a co-reductant, which provides two electrons per one molecule of the product. There were also successful attempts to employ hydrogen sulfide as the reducing agent in like reactions [6,7].

Metalloporphyrins, especially electron-deficient, can act as oxygenation catalysts in abiological systems that do not require any reductants at all and use both oxygen atoms from the O_2 molecule [8–10]. Interestingly, ethylbenzene oxidation by dioxygen, catalysed by iron(III) tetrakis(pentafluorophenyl)porphyrin, under similar conditions, gave the very same products (1-phenylethyl hydroperoxide, 1-phenylethanol and acetophenone) [11] as oxidation of styrene catalysed

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by iron(III) porphyrins in the presence of reductants [12].

Thiols and olefins can give a variety of products. Under typical radical reaction conditions, for instance under UV irradiation, they yield anti-Markovnikov addition products [13]. An interesting class of reactions are thiol-olefin co-oxidation (TOCO) reactions occurring in hydrocarbon solutions when a stream of air is passed through them [14]. The principal products of the TOCO reactions are substituted 2-mercaptoethylhydroperoxides that rearrange at room temperature yielding substituted 2-sulfinylethanols. Other products are the anti-Markovnikov addition product and the respective disulfide. It had generally been accepted that the TOCO reactions are initiated by a thyil radical produced from thiols until the process had been carefully studied by Szmant and co-workers [15]. They also demonstrated that the main role plays a charge transfer complex formed by co-ordinating the thiol through its sulfur atom to the double bond of the olefin or the aromatic ring [16].

In literature, there are two examples of the reaction between styrene and benzenethiol in the presence of iron porphyrins described, both from the same laboratory. When the reaction is carried out in an inert atmosphere, and benzenethiol is generated in situ from diphenyl disulfide and borohydride, then it gives the Markovnikov addition product in rather low yields [17]. Another example describes the use of benzenethiol to modify the iron porphyrin centre in the catalytic oxidation of styrene [18]. The thiol was also produced in situ by reduction of the disulfide with borohydride. Beside ordinary products of the oxidation of styrene in the presence of metalloporphyrins and borohydride, like 1-phenylethanol and acetophenone, benzyl alcohol was detected in the reaction mixture. It was believed that it was formed from benzaldehyde upon the reduction by borohydride.

In the present work, we have studied the oxidation of styrene in the presence of iron porphyrins and thiols in an alcohol, methoxyethanol. The major products of the reaction were benzaldehyde and a methyl sulfide, in which the second substituent comes from the thiol used. The side products were the appropriate disulfide and the anti-Markovnikov addition product (not present in the case of alkyl thiols). An aryl thiol, benzenethiol, gave the most active system. Alkyl thiols were far less active, the least yields were ob-

tained with hydrogen sulfide. Therefore, detailed studies were carried out for the oxidation of styrene in the presence of benzenethiol. Though the thiols were used in amounts needed for acting as co-reductants, i.e. providing two electrons per one oxygen atom inserted, it appeared that they cannot be treated as such. In some systems, the quantity of appropriate disulfide formed (the product of oxidation of thiols) was insufficient for such a course of the reaction. The reaction towards benzaldehyde proceeded only in the presence of iron porphyrins. After their degradation, the oxidation of styrene stopped, then, in the case of the system with benzenethiol, the addition reaction and disulfide production proceeded even with enhanced rates.

2. Experimental

The solvent, methoxyethanol (Merck–Schuchardt), and styrene (Riedel–Haën) were distilled once a week and stored afterwards in a freezer. Thiols (Aldrich and Fluka) were used freshly distilled for the reaction. Iron tetraphenylporphyrin chloride was obtained by standard literature methods [19]. It was periodically recrystallised from dichloromethane/hexane after shaking its dichloromethane solution with a saturated NaCl solution that was slightly acidified with HCl. 2-Phenylthio-1-phenylethyl hydroperoxide was obtained from benzenethiol and styrene in hexane at $0\,°C$, as described in literature [14]. It was used as obtained in the form of oil containing 80% of the hydroperoxide.

The reactions were carried out in a thermostated ($25\,°C$) glass reactor of 15 mm diameter and 85 mm overall height, which was fitted with a 14/23 standard ground joint. The reactor was open to the air, if not otherwise noted. The reaction mixture was stirred with a magnetic stirrer at a rate of 500 rpm. In all the reactions, the following sequence of adding reagents was obeyed: first, the catalyst was added to the solvent (generally $5\,cm^3$), next cyclohexanol (internal standard), then styrene and finally, after about 1 min, the thiol. The adding of the thiol marked the start of the reaction. At time intervals, aliquots were taken for GLC analysis and UV-Vis spectra. The samples taken for recording the spectra were returned to the reactor. To make sure that the reaction is not affected by light, the reactor was wrapped with black paper in some cases.

There were no differences noticed between the reactions protected from light and exposed to it.

GLC analyses were carried out with a Hewlett-Packard Series II 5890 instrument equipped with a FID and Stabilwax 30 m capillary column. In order to detect benzoic acid in the products, a sample of the reaction mixture was treated with an excess of a diethyl ether solution of diazomethane. Prior to that it was confirmed by adding a known quantity of benzoic acid to a sample of the reaction mixture that the method can be used for quantitative determination of benzoic acid in mixtures of such composition.

Electrochemical analyses were performed with a Bioanalytical Systems Model BW100 Electrochemical Analyser in a conventional three-electrode cell. BAS platinum disk and glassy carbon electrodes were used as working electrodes, Pt wire as an auxiliary electrode and the potentials were measured against an Ag/AgCl (3 M NaCl) reference electrode.

UV-Vis spectra were recorded with a Hewlett-Packard 8453 Spectrophotometer equipped with a diode array detector in 1.0, 0.5 and 0.1 cm quartz cuvettes.

3. Results and discussion

3.1. General (the activity of various types of thiols)

Three types of thiols were examined, a primary alkyl thiol, ethanethiol, a secondary alkyl thiol, cyclohexanethiol and an aromatic thiol, benzenethiol, and hydrogen sulfide. Iron(III) tetraphenylporphyrin chloride was employed as the catalyst. The reactions were carried out in methoxyethanol solutions at 25 °C. In a part of the studies, the concentration of the porphyrin as high as 1 mM was employed. The iron porphyrin itself did not dissolve in such a high amount in methoxyethanol, but after adding thiols, the system quickly homogenised.

The major products of the oxidation reaction were benzaldehyde and an appropriate methyl sulfide formed from the respective thiol. Both products were always produced in the same molar ratio from the beginning of the reaction, though the value of this ratio varied (between 1.4:1 and 1.0:1) depending on the reaction conditions:
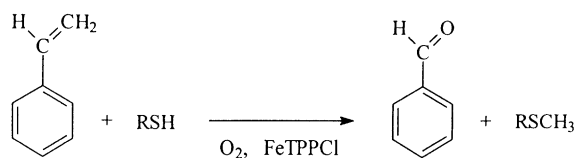
Other products were the appropriate disulfide RSSR and the anti-Markovnikov addition product formed only with the aryl thiol, benzenethiol (PhCH$_2$CH$_2$SPh). Alkyl thiols did not give addition products. It should be stressed that benzaldehyde and the methyl sulfide were produced only in the presence of iron porphyrin. When it was degraded to a red-brown species, resembling in colour ferredoxin type iron thiolate sulfide complexes, the systems with alkyl thiols completely lost their activity, but in the system with benzenethiol disulfides and addition products were still formed. In UV-Vis spectra, the Soret and other distinctive bands in the visible region, characteristic of the porphyrin, disappeared at that time, leaving only a broad band sloping off to longer wavelengths. No other products of the oxidation of styrene, particularly those characteristic of other porphyrin systems, like acetophenone or 1-phenylethanol were discovered in the reaction mixture. Benzaldehyde was not further oxidised in the system. No traces of benzoic acid were found. In the reaction with benzenethiol, traces of bis(phenylthio)methane, PhSCH$_2$SPh, were also detected among the products.

As can be seen from Table 1, the best results were clearly obtained with the aromatic thiol, benzenethiol. Interestingly, hydrogen sulfide gave also benzaldehyde as the product of the oxidation. Turnover number (TON) value of 4 refers to hydrogen sulfide introduced in a manner similar to other thiols, i.e. 2 mol/mol styrene, at the beginning of the reaction. When H$_2$S was passed continuously through the solution in a

Table 1
Benzaldehyde yield and turnover numbers for thiols and hydrogen sulfide

Thiol/H$_2$S	Benzaldehyde yield (%)	TON
Benzenethiol	46	180
Cyclohexanethiol	6.3	25
Ethanethiol	3.8	15
H$_2$S	0.9	4 (28)

[FeTPPCl] = 1.0 mM; [styrene] = 0.4 M; [thiol] = 0.8 M; [H$_2$S]—see text.

mixture with air, the higher yield (TON = 28) was obtained. Respective methyl sulfides (cyclohexyl methyl and ethyl methyl sulfide) accompanied benzaldehyde in ca. equimolar amounts. In the case of benzenethiol, under the conditions from Table 1, the molar ratio of benzaldehyde to methyl phenyl sulfide was equal 1.3:1. The major products of the reaction with alkyl thiols were respective disulfides.

3.2. Reaction in the presence of benzenethiol

Further detailed studies were carried out with benzenethiol only. Selected representative results are summarised in Table 2. Usually the reactions proceeded for about 4 h unless the catalyst degraded earlier. In most cases the conversion of styrene was beyond 90% and it reacted towards chromatographically detected products (benzaldehyde and addition product) in about 60%. Interestingly, benzenethiol generally gave 85% of chromatographically detected products (disulfide, sulfide and addition product). Most probably, the major side reaction was styrene polymerisation that proceeded at a later stage of the reaction, as in the first stage (fast reaction at the beginning), about 90% of styrene and its products were analysed chromato-

graphically. There were no significant differences found between reactions with 1.0 and 0.5 mM catalyst concentration. The system with a lower concentration of catalyst (0.1 mM) yielded 92 and 95% of chromatographically analysed products from styrene and benzenethiol, respectively. The major product in the latter system was though the anti-Markovnikov addition product. Significantly lower yields of detected products (25% of styrene and 73% of thiol) were obtained in reaction no. 4 of Table 2, in which a strong stream of air was passed on to the surface of the solution causing evaporation of a part of solvent. In reaction no. 2, in which a gentle stream of air was passed on to the surface of solution, the total concentration of found products from styrene was also lower (42%).

The kinetics of the reaction, as can be seen from Fig. 1, is very complex. At the start, a jump occurred, during which ca. 15% of styrene reacted. This jump occurred only when higher concentrations of the catalyst and the thiol were used. Next, the reaction slowed down and after a while, it accelerated again. The ratio of benzaldehyde to methyl phenyl sulfide changed slightly during the reaction. Generally, this ratio was equal 1.1:1 at the beginning, then increased to 1.3:1. The amount of the addition product was also low in

Table 2
Selected results of the reactions with benzenethiol

Reaction no.	Initial concentration			Conversion[a,b] (%)	Selectivity towards PhCHO[b,c] (%)	[PhCHO]/ [PhSMe][b]	TON[d]	[PhSSPh]/ [PhCHO][e]	Remarks
	FeTPPCl (mM)	Styrene (M)	Thiol (M)						
1	1.0	0.4	0.8	91	50	1.3	180	0.95	
2	1.0	0.4	0.8	99.5	42	1.2	160	0.80	With air introduced on to the surface
3	0.5	0.4	0.8	96	37	1.3	310	0.68	
4	0.5	0.4	0.8	99	19	1.0	144	1.30	With strong stream of air (solvent partly evaporated)
5	0.5	2.0	0.8	35	32	1.2	380	0.26	
6	0.1	0.4 (+0.4)	0.8	99 (85)	15 (12)	1.0	640 (830)	0.90 (0.60)	Numbers in parentheses refer to the overall results after the addition of the second portion of styrene

[a] Conversion calculated as % of styrene reacted.
[b] At the end of reaction.
[c] Selectivity calculated as % of [benzaldehyde]/[styrene reacted] ratio.
[d] Turnover number calculated only for benzaldehyde.
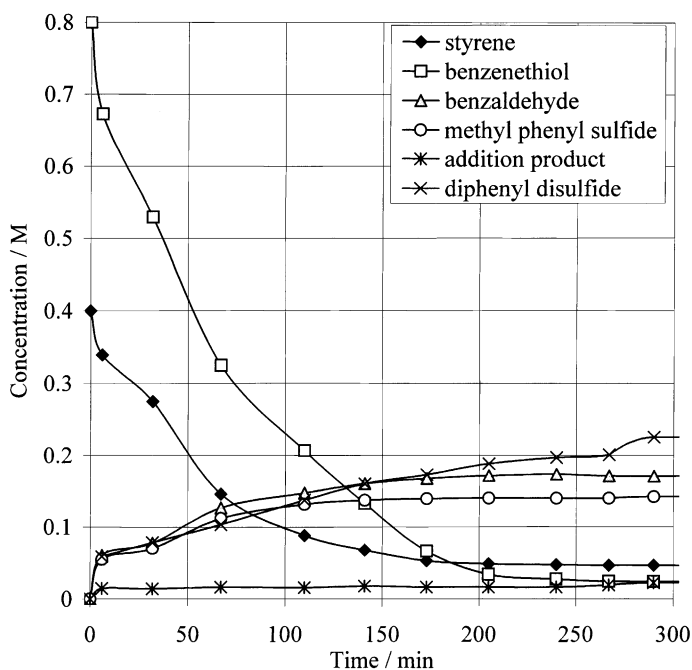[e] In the middle of reaction—at the end of reaction this ratio was generally higher.

Fig. 1. Reaction mixture composition vs. time for the reaction in the presence of benzenethiol and FeTPPCl (1 mM).

general. Diphenyl disulfide is produced in equimolar amounts to methyl phenyl sulfide at first, though after some time its yield increases with the degradation of the catalyst. A rapid increase is observed at the end of the reaction, when there is virtually no porphyrin in the system. Still, particularly at the beginning of the reaction, the amount of the disulfide is too low to account for a typical cytochrome P-450 model system with a sacrificial reductant. Its amount in such a case should be equimolar to at least the amount of benzaldehyde formed. In some cases (reaction no. 5 of Table 2), the ratio of its concentration to the concentration of benzaldehyde remained as low as 0.26 during the total period of the reaction. In this case we found 82% of products from benzenethiol, which means that the thiols do not act as sacrificial reductants in the system studied.

In most of the above described experiments, the reactors were simply open to the atmosphere and the solutions were stirred with a magnetic stirrer (500 rpm) to enable a free flow of oxygen by diffusion. The jump observed at the start of the reaction indicated that the further retardation of the reaction might be due to a lower concentration of oxygen in the reaction solution. We tried therefore to increase its flow by forcing it directly above the surface of it. It led to speeding up the degradation of the catalyst and lower overall yields of benzaldehyde. Characteristic of those reactions is also a higher yield of diphenyl disulfide.

Dividing the portion of the thiol did not help, either (Fig. 2). At the beginning, the system seemed to be as active as before but did not enter the second stage of activity, probably because the thiol reacted. In the previous case (Fig. 1), 0.2 M benzenethiol also reacted after 50 min. There are no signs of the degradation of the porphyrin (vide infra) and no clear differences in the spectra between these two cases. The system recovered its activity after the addition of a further amount of the thiol. The overall yield of benzaldehyde is though lower (42% selectivity at 95% styrene conversion).

Lowering the starting concentration of the porphyrin led to lower selectivities of the reaction. Still, at the concentration of 0.5 mM, the main reaction was the production of benzaldehyde. When the concentration of the catalyst was as low as 0.1 mM (reaction no. 6 of Table 2), then, from the start on, the main reaction
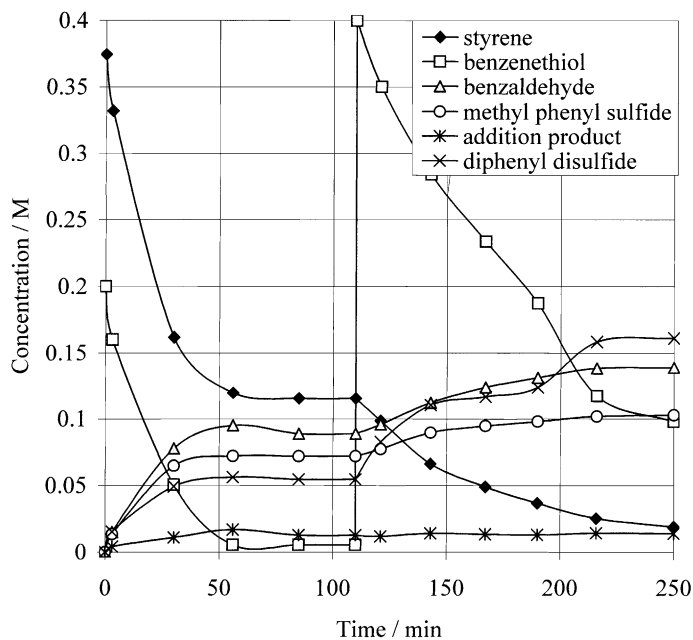
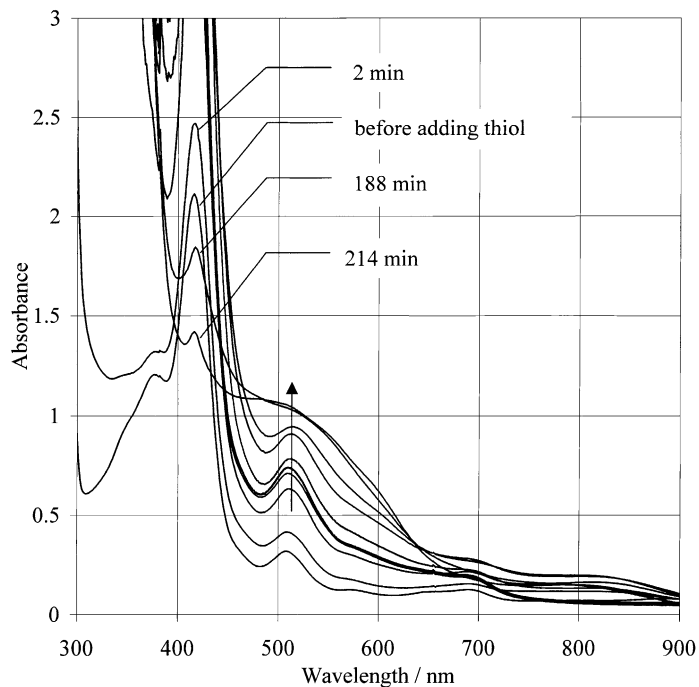Fig. 2. Reaction with thiol addition divided into two portions ([FeTPPCl] = 1 mM).

Fig. 3. UV-Vis spectra of the reaction system from Fig. 2 recorded in 0.1 cm cuvettes; spectra taken after 2, 25, 51, 111, 136, 163, 166, 188 and 214 min reaction time.

was the anti-Markovnikov addition. The ratio of benzaldehyde to methyl phenyl sulfide was 1:1 at the beginning and remained so till the end of the reaction. In this case, the yield of benzaldehyde was substantially lower as compared to reactions with a higher concentration of the porphyrin, but interestingly, the calculated turnover number (830) increased almost five times as compared to 1 mM porphyrin concentration. It indicates, how misleading quoting results only in terms of TONs might be. Under these reaction conditions, after the degradation of the catalyst, the thiol itself was not oxidised to disulfide. The addition of a further amount of styrene at this moment, however, produced almost instantly the anti-Markovnikov addition product. This indicates a difference in the activity of the degraded catalyst. At a higher concentration, it is active towards the oxidation of thiols to disulfides, at low concentrations though, it promotes the addition reaction. We observed that this latter reaction is catalysed even by traces of iron compounds. It was almost impossible to prepare standard mixtures for GLC containing both styrene and benzenethiol in flasks that were previously contacted with an iron porphyrin solution and not cleaned scrupulously with a hot 'piranha' solution.

3.3. UV-Vis spectra

The reactions were followed by UV-Vis spectra. Figs. 3 and 4 illustrate the spectra recorded for the reaction of Fig. 2.

There were no dramatic changes in the spectra. All the bands characteristic of the starting iron tetraphenylporphyrin chloride are seen almost until the end of the reaction. The Soret band remained at the same position of 416 nm but broadened, which might indicate a split of it (seen indeed in differential spectra). During the reaction, a broad, almost featureless absorption, descending towards longer wavelengths, developed. Decreasing absorption intensity in the Soret band, without any other band being formed in the region expected for the Soret band indicates the degradation of the porphyrin. The course of this degradation was not always consistent. At higher porphyrin concentrations, the degradation occurred suddenly at some point of the reaction. At lower concentrations of the catalyst it generally occurred gradually. The degradation was faster, when the air was introduced into the solution or directly on to the surface of it, which apparently was the reason of lower overall yields.
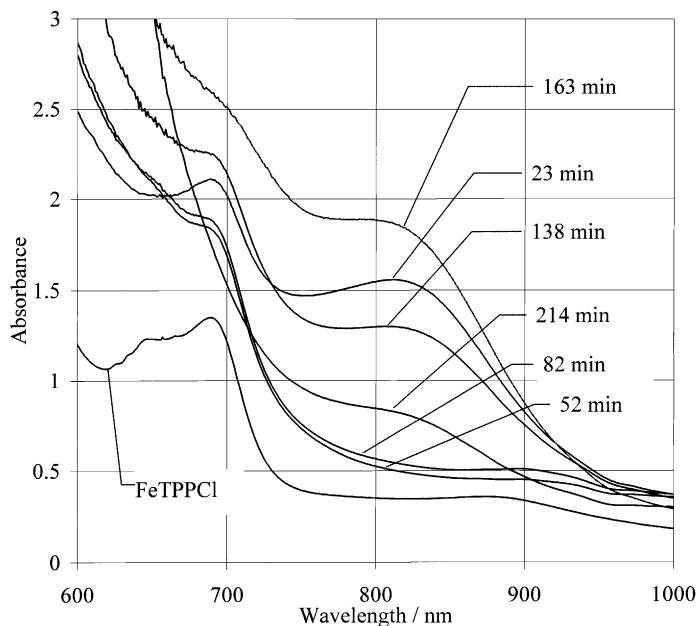

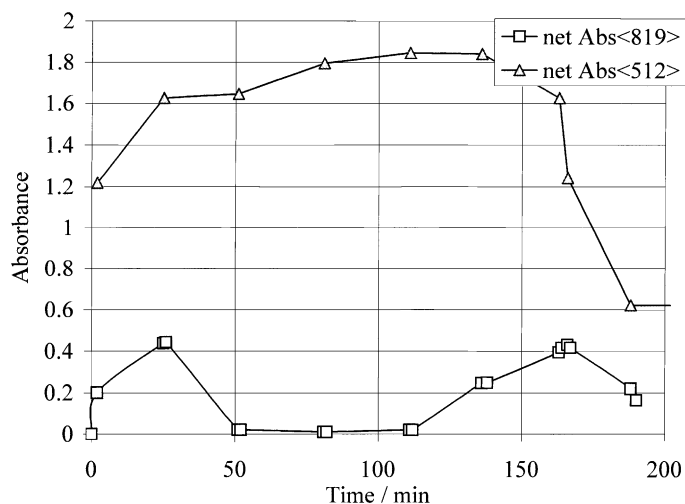Fig. 4. UV-Vis spectra of the reaction from Fig. 2 recorded in 1 cm cuvettes.

Fig. 5. Variation of corrected values of absorbance at 819 and 512 nm with time for the reaction of Fig. 2.

The most interesting feature is the appearance of a new band at 819 nm during the active phase of the reaction. It is seen in the spectra in Fig. 4. Because of its position at such a long wavelength it was easily identified. As can be seen from Fig. 4, it appeared at the beginning of the reaction, then disappeared when the reaction stopped because of the consumption of the thiol and reappeared after the addition of the new portion of the thiol. It is better seen in Fig. 5 showing corrected absorbances for the 819 nm band in time. In the same figure, corrected intensities of the 512 nm band are shown. They can be related to the fate of the porphyrin (the increase in the intensity observed at the beginning is due to dissolution of the porphyrin). The intensity of the Soret band was too high to be used for this purpose. The maximum intensity of the 819 nm band was higher in the reactions with higher initial concentrations of the porphyrin and styrene. The band disappears though when the concentration of benzenethiol falls below a certain limit (ca. 10 mM at the initial concentration of the catalyst 1.0–0.5 mM). The absorbance at 819 nm cannot be correlated with the reaction rate directly. The band intensity rises with time to a certain maximum to fall down faster afterwards. The highest reaction rate is observed at the beginning of the reaction or right after the addition of the second portion of the thiol, as in the example of Fig. 2. This means that the 819 band is not due to a direct reaction intermediate. It is rather due to a species being in equilibrium with a reaction intermediate, an intermediate being formed with some delay. According to literature [20], this band is due to iron(III) porphyrin radical cation, Fe(III)TPP$^{+\bullet}$. Other bands characteristic of this species (397, 530 and 600 nm) [20–22] can also be spotted in the spectra but they are overlapped by other stronger bands. The 530 and 600 nm bands (the latter one as a shoulder) are seen in the differential spectra.

3.4. Reaction of iron porphyrins with benzenethiol in methoxyethanol

It was also interesting to see spectral changes in the reaction of iron porphyrins and benzenethiol in methoxyethanol. The reaction was described years ago [23–25] but the starting porphyrin was μ-oxo dimer (FeTPP)$_2$O and it was studied in other solvents (benzene, toluene). Obtained complexes were generally unstable, complexes with more electronegative (usually aromatic) thiolate ligands showed higher stability [26]. It is known from literature that in the first stage of the reaction of benzenethiol with the μ-oxo dimer is a thiol–thiolato complex, FeTPP(SPh)(HSPh) [24], then iron is reduced yielding FeTPP, which in turn can be oxidised with dioxygen to give back the μ-oxo dimer [23].

We carried out the reactions in a spectrometer cuvette and started them under argon atmosphere. It appeared that FeTPPCl behaved differently from

(FeTPP)$_2$O. Only the latter one gave immediate dramatic changes in the spectra upon the addition of a 10-fold excess of benzenethiol to saturated solutions of the iron porphyrins in methoxyethanol. New bands that appear at 535–540, 610 (shoulder) and 714 nm (broad) are common to both the chloro complex and μ-oxo dimer. The two former bands can most probably be ascribed to a bis(methoxyethanol) complex, Fe(II)TPP(MeOCH$_2$CH$_2$OH)$_2$ [17]. They rise upon the addition of further amounts of the thiol (up to 100-fold excess). The changes need a few minutes time to develop. In the case of FeTPPCl, though, up to 95% of the initial spectrum can be subtracted, which means that either there is still so much of the starting porphyrin present in the mixture or a product of almost identical spectrum is formed. This latter situation seems likely as pentacoordinate thiolate complexes formed by substitution of the axial chloride by PhS$^-$ have almost identical spectra to the chlorides [27]. Such complexes are not formed in the case of the μ-oxo dimer. Further changes are observed when the air has been introduced into the solution. In the case of FeTPPCl, the bands at 570 and 601 nm decrease but the broad one at 710 nm increases. The last one increased also after the addition of the air in the case of (FeTPP)$_2$O.

It is clear that the reactions proceed differently in the case of both porphyrins. In the case of the chloro complex FeTPPCl, the final product after exposing the reaction mixture to the air is not the μ-oxo dimer, as suggested by the literature.

3.5. Reaction of 2-phenylthio-1-phenylethyl hydroperoxide in the presence of iron porphyrin

It is known that benzenethiol and styrene in the presence of the air spontaneously form 2-phenylthio-1-phenylethyl hydroperoxide, PhSCH$_2$CH(OOH)Ph [14]. The hydroperoxide is unstable at room temperature and rearranges yielding 2-phenylsulfinyl-1-phenylethanol, PhS(O)CH$_2$CH(OH)Ph. On the other hand, the hydroperoxide contains building blocks of benzaldehyde and methyl phenyl sulfide, hence it is plausible that these two products are formed from the hydroperoxide spontaneously formed in the solution, which would be next cleaved homolytically by the iron porphyrin. In order to check it we added 0.30 M of the hydroperoxide into a solution of 1 mM

FeTPPCl in methoxyethanol. The reaction was followed by UV-Vis spectrometry and GLC. No products that could be identified chromatographically were formed in this reaction. There was no trace of neither benzaldehyde nor methyl phenyl sulfide. The reaction was repeated with benzenethiol added with the same negative result. It is clear that the studied reaction of oxidation of styrene does not proceed through the cleavage of the hydroperoxide formed spontaneously in the solution.

UV-Vis spectra of the reaction mixture after the addition of the hydroperoxide indicated formation of a complex strongly absorbing in the UV with a featureless slope in the visible region. Since the start of the reaction, peaks in the visible region characteristic of the starting porphyrin diminished (to ca. 35% of their initial intensity) and new ones protruding above the slope appeared at 570 and 611 nm with the intensity ratio of about 2:1 (characteristic of μ-oxo dimer (FeTPP)$_2$O [28]). Rough comparison of the intensities of the bands would indicate that about 30% of the initial FeTPPCl was converted into the μ-oxo dimer. After 70 min the tendency was reversed and the peaks characteristic of FeTPPCl restored, while those at 570 and 611 nm diminished. At the end of the reaction (after 120 min), the spectrum resembled the initial one with rather strong, but featureless background added. Characteristically there were no peaks in the longer wavelength region (beyond 750 nm). In such a reaction one would expect the formation of ferryl porphyrins. They give characteristic spectra that should have been observed in this reaction but have been not. It is unclear how it came about to the formation of the μ-oxo dimer, which in turn, at the end of the reaction was converted back to the chloro complex. Such a reaction is known to occur but in the presence of an excess of chlorides; μ-oxo dimer is formed in the presence of bases, on the other hand.

3.6. Attempted reaction of styrene oxide in the iron porphyrin–thiol system

Styrene oxide proved to be almost inert in the iron porphyrin–benzenethiol system (1 mM FeTPPCl, 0.4 M styrene oxide and 0.4 M benzenethiol in methoxyethanol). After an overnight reaction 80% of it was recovered unreacted (after 2 h, 95%). Only traces (<0.1% of the initial styrene oxide amount)

of benzaldehyde and no methyl phenyl sulfide were found in the reaction mixture. Benzenethiol was virtually quantitatively oxidised to disulfide. No other products could be found chromatographically. This and the fact that no traces of it were found in styrene oxidation reaction mixtures proves that styrene oxide can be excluded as an intermediate in the oxidation of styrene in the studied system.

3.7. Electrochemical reduction of iron porphyrin complexes in methoxyethanol

In order to check the influence of substitution of chlorides by thiolates on to the reduction potential of iron porphyrin in methoxyethanol, the solvent used, cyclic voltammograms were registered in it. To ensure the reversibility of the substitution, tetramethylammonium chloride was employed as the supporting electrolyte.

As can be seen from Fig. 6, $E_{1/2}$ for FeTPPCl is equal to −0.17 V and the cathodic peak appears at −0.21 V. After addition of benzenethiol a new broader reduction wave is formed at −0.36 V but at the same time the peak of the former reduction is shifted by 0.01 to −0.22 V. This means that the potential of the newly formed species is shifted cathodically by 0.14 V. Upon adding an excess of benzenethiol the peak of the thiolato complex is shifted even more cathodically to −0.41 V. This shift corresponds to a 0.18 V cathodic shift observed for a benzylthiolate iron porphyrin complex [1]. Interestingly, in Fig. 6, there is only one common oxidation peak. Analogously to the reaction sequence proposed for the reduction of iron porphyrin chloride [29], this behaviour can be explained by the following reaction:

$$FeTPP(SPh) \xrightarrow{e^-} FeTPP(SPh)^-$$
$$\xrightarrow{e^-, +Cl^-} FeTPPCl^- + SPh^-$$
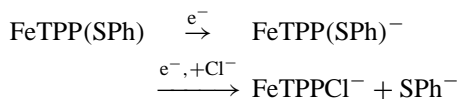
Interestingly, at low scan rates, the reduction peak of the thiolate complex disappears. It might be due to an equilibrium between the chloride and thiolate complexes. In the vicinity of the electrode, the chlorides undergo first the electrode reaction, their concentration decreases, hence, due to the equilibrium the thiolates
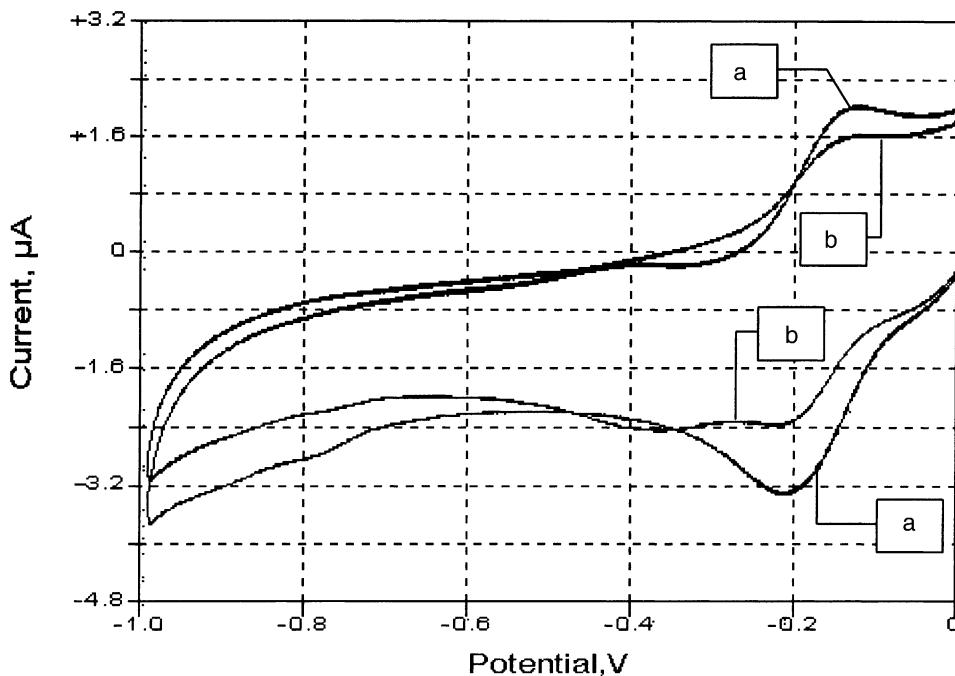

Fig. 6. Cyclic voltammogram of 0.5 mM FeTPPCl in methoxyethanol (0.1 M Me₄N·Cl) prior to (a) and after adding 2 mM benzenethiol (b); (potential vs. Ag/AgCl); scan rate 100 mV/s.

are converted into chlorides in terms of the excess of chloride anions from the supporting electrolyte.

Cyclic voltammetry after the addition of the air and styrene revealed nothing interesting for catalysis. Iron porphyrins proved to catalyse the reduction of dioxygen, but after the addition of benzenethiol the O_2 reduction seems to be more sluggish. The addition of styrene to the solution decreases the O_2 reduction currents due to fast consumption of oxygen in the styrene oxidation reaction.

Thus there might be two conclusions related to catalysis drawn from electrochemistry: benzenethiolate is a better electron donor than chloride, and chloride and benzenethiolate complexes are in equilibrium with each other; a new equilibrium state sets quickly in the cyclic voltammetry time scale.

4. Conclusions

Thiols promoted the oxidation of styrene catalysed by iron porphyrins to benzaldehyde and a methyl sulfide. The reaction proceeded only in the presence of iron porphyrins. The most active thiol appeared to be an aryl thiol, benzenethiol. The ratio of the major products, benzaldehyde and methyl phenyl sulfide generally was equal to 1.1:1 at the beginning of the reaction to increase to 1.3:1 at the end of it. During the active phase of the reaction, iron(III) porphyrin cation radical was detected in the UV-Vis spectra. It does not make the intermediate of the reaction as its concentration does not correspond with the rate of the reaction. It seems as though it were in equilibrium with an intermediate but formed with a delay.

It is plausible that benzaldehyde and methyl phenyl sulfide can be formed from 2-phenylthio-1-phenylethoxy radical, $PhSCH_2CH(O^\bullet)Ph$, by β-scission. It is also confirmed by the presence of traces of bis-(phenylthio)methane, $PhSCH_2SPh$, in the reaction mixture. That radical can in turn come from a homolytic cleavage of 2-phenylthio-1-phenylethyl hydroperoxide, which is readily formed from a π-complex of benzenethiol and styrene (the participation of porphyrin, also an aromatic system, in the complex cannot be excluded). It was proven though that the hydroperoxide formed spontaneously in the solution does not yield the former two products under the reaction conditions. However, one cannot exclude

homolytic cleavage of the hydroperoxide formed on the iron centre or just generally with the participation of the porphyrin. A second product of the homolytic cleavage would be a hydroxy iron complex with iron valence raised by one, i.e. to Fe(IV). It could act as an oxygen donor to an olefin molecule. With styrene this would eventually yield benzaldehyde. Hence, we would have a second molecule of benzaldehyde on top of the first one obtained from the β-scission. The slight increase in the molar ratio of benzaldehyde to methyl phenyl sulfide during the course of the reaction and somewhat lower ratios than 2:1 indicate that the excess benzaldehyde could be formed in free radical reactions initiated by either phenylthiomethoxy radical, $PhSCH_2O^\bullet$, or other radicals formed from Fe(IV) porphyrin, the second product of the homolytic cleavage. Iron(IV) porphyrin complex proposed in this scheme was not detected in the reaction mixture, but iron(III) porphyrin radical cation, seen in the spectra, might come from an electron transfer from iron(IV) to the porphyrin ring. It was shown that the iron(III) porphyrin cation radical is not a direct intermediate in the oxidation reaction. It is formed with a delay and is probably in equilibrium with an intermediate.

It was demonstrated recently that electron donor ligands promote homolytic cleavage rather than heterolytic, as it had been believed for a long time [30,31], and benzenethiol acts indeed as an electron donor, as shown by electrochemistry. Additionally, the hydroperoxide contains sulfur substituents, which also contribute to the tendency towards homolytic cleavage, as does the fact that tetraphenylporphyrin is a relatively electron rich porphyrin [30]. The participation of peroxo iron complexes, recently postulated in literature [32], is unlikely as in this case they would yield acetophenone that was not detected.

The reaction seems to be controlled to some extent by diffusion of oxygen. On the other hand, supplying oxygen (air) more efficiently ends up in the degradation of the catalyst and lower yields. It is apparently due to an uncontrolled radical reaction initiating also styrene polymerisation. The desired reaction of oxidation is catalysed by iron porphyrin. It is plausible that until the reaction proceeds within the solvent cage containing also an iron porphyrin then it yields benzaldehyde and methyl phenyl sulfide. When the concentration of oxygen is high, then the radicals are

formed in higher amounts and undesirable reactions could be initiated.

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