



Co-oxidation of styrene and *iso*-butyraldehyde in the presence of polyaniline-supported metalloporphyrins

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Abstract

Co-oxidation of styrene and *iso*-butyraldehyde with gas phase oxygen in the temperature range 20–35 °C has been studied in the presence of Co-, Fe- and Mn-T(*p*-SO₃H)PP porphyrins in the liquid phase and supported on polyaniline (PANI) as catalysts. The reaction is proceeding along two parallel pathways: formation of benzaldehyde and epoxystyrene with products of its tautomeric isomerization, mainly phenylacetaldehyde. *iso*-butyraldehyde is mediating the transfer of oxygen from the gas phase to styrene through generation of radicals by interaction with the porphyrin molecules and formation, by reaction with oxygen molecules, *iso*-butyrylperoxy radicals. Supporting the porphyrin molecules on polyaniline modifies their catalytic properties. The mechanisms of the two parallel reaction pathways to benzaldehyde and epoxystyrene + phenylacetaldehyde are discussed.

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1. Introduction

Homogeneous catalytic reactions carried out in the liquid phase offer many advantages as compared to gas phase heterogeneous catalytic processes. They can be carried out in mild conditions with relatively high rates because of easy access of reactant molecules to the active sites of molecularly dispersed catalyst and therefore enable the achievement of high chemo-, regio- or stereoselectivity. Liquid phase oxidations in the presence of transition metal complexes as catalysts at the difference with hydrogen peroxide and organic hydroperoxide, proceed by a chain mechanism, the primary products of the oxidation of hydrocar-

bons being alkyl hydroperoxides, and in many cases require the addition of a sacrificial co-reductant. In contrast, in gas phase oxidations the chain reaction leads to total oxidation products and must be avoided, because selective oxidation can be obtained only as a result of redox mechanism, in which nucleophilic addition of oxide ions to the activated hydrocarbon molecule takes place.

The group of catalysts active in homogeneous oxidation, widely studied in recent years, are metalloporphyrins, because of the perspective of their application as catalysts in selective oxidation of hydrocarbons and their derivatives [1–3]. They are also model systems for studies of the mechanism of mild oxidation of organic compounds in the liquid phase by such biocatalysts as monooxygenase cytochrome P-450. There are, however, several disadvantages in using metalloporphyrins as catalysts in oxidation processes.

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They are difficult to separate from the products after the reaction has been completed and therefore there is no possibility to implement a continuous process. Some metalloporphyrins easily undergo dimerization, the dimer being inactive in the reaction. Finally, some simple porphyrin ligands may become oxidized in the reaction medium, which results in the destruction of the catalyst; fortunately, recent polyhalogenated or polynitrated ligands proved to be very stable. One of the methods to circumvent these disadvantages is deposition of the porphyrin on a support, which simultaneously has the advantage of turning the liquid phase oxidation from homogeneous into heterogeneous. Various supports have been tried: inorganic as, e.g. zeolites [4–6] and organic as polymers [7–9]. In the present paper, we report the results obtained in co-oxidation of styrene and *iso*-butyric aldehyde by gas phase oxygen in the presence of Fe, Co and Mn porphyrins, supported on polyaniline (PANI), as catalysts. This type of co-oxidation was first studied by Mukaiyama and co-workers [10,11].

2. Experimental

2.1. Materials

2.1.1. Metalloporphyrins

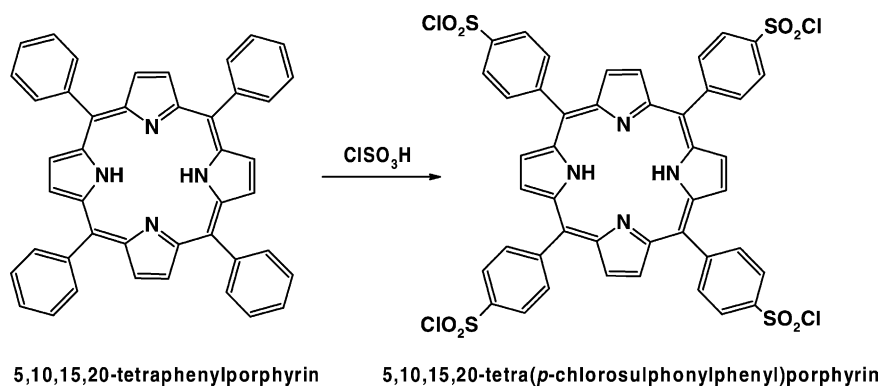
Tetraphenylporphyrin (H_2TPP) was synthesized by boiling in nitrogen the solution of pyrrole and benzaldehyde in propionic acid for 1.5 h and slow cooling [12]. The precipitated crystallites of H_2TPP

were filtered, washed with methanol and water, and dried. In order to enable binding to polyaniline as the support porphyrin had to be functionalized by introduction of proper functional groups to the phenyl rings.

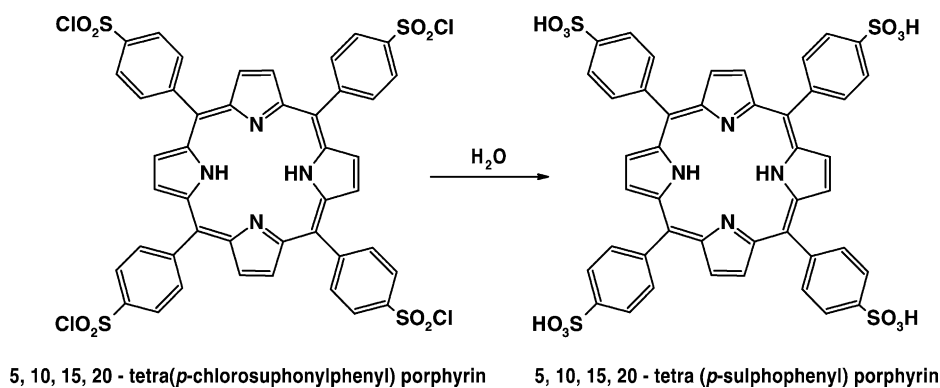
This was achieved by chlorosulphonation (Scheme 1) [13]. H_2TPP was mixed with chlorosulphonic acid ($ClSO_3H$) for 1 h at room temperature and the solution was slowly poured on ice. Then saturated solution of sodium carbonate was added until neutralization of the solution. The resulting $H_2T(p-SO_2Cl)PP$ was extracted with chloroform and after evaporation of the solvent it was transferred to the container, attached to a reflux condenser, and refluxed with water for 12 h in order to hydrolyze the SO_2Cl groups to obtain the required SO_3H groups (Scheme 2). Water was then evaporated and the solute left to dry.

The metallation of the 5,10,15,20-tetra(*p*-sulphophenyl)porphyrin ($H_2T(p-SO_3H)PP$) to obtain $MT(p-SO_3H)PP$ was carried out in a following way.

- *Introduction of iron:* $H_2T(p-SO_3H)PP$ was mixed with water, powdered iron was added and the mixture was refluxed for 1 h. The process of metallation was followed by UV-Vis spectrometry by observation of the change of the Soret band. The resulting crystallites were then washed with methanol.
- *Introduction of cobalt and manganese:* $H_2T(p-SO_3H)PP$ was reacted with cobalt or manganese acetate, respectively by refluxing for 1 h. The reaction was checked by following the change of Soret band and the resulting crystallites were washed with methanol.



Scheme 1. Synthesis $H_2T(p-SO_2Cl)PP$.

Scheme 2. Hydrolysis $H_2T(p-SO_2Cl)PP$.

2.1.2. Preparation of metalloporphyrins supported on polyaniline

Polyaniline was synthesized by oxidative polymerization of aniline in the presence of sodium persulphate in the hydrochloric acid solution [14]. Polyaniline exists in three principal forms leucoemeraldine, emeraldine and pernigraniline. After the reaction the short chains of the polymer were separated by extraction with acetone and the polymer was deprotonated by treatment with ammonia to obtain emeraldine.

The supported porphyrin catalysts were prepared by proton exchange between the $MT(p-SO_3H)PP$ and the emeraldine base in a following way. A solution (1.5 mole/dm^3) of $MT(p-SO_3H)PP$ was added dropwise to the mixture of polyaniline and water until the colour of the solution ceased to disappear. Small excess of porphyrin was then added and the mixture was left under stirring for 24 h. The polymer was then separated from the solution by filtering and dried over the silica gel. The amount of porphyrin deposited was calculated by subtracting the amount of porphyrin remaining in the filtrate from the amount of porphyrin introduced to the reaction. In the case of supported cobalt porphyrin three samples were prepared, containing 150, 270 and 460 monomers per one porphyrin molecule (the content of porphyrin amounted to 6.8, 4.0 and 2.4 wt.%, respectively), in the case of iron and manganese porphyrins the catalysts contained 3000 and 130 monomers per one porphyrin molecule (the content of porphyrin amounted to 0.36 and 8 wt.%, respectively).

The way of fixing the porphyrin molecules to the polyaniline support was determined by using FTIR spectroscopy. Fig. 1a shows the IR spectrum of $CoT(p-SO_3H)PP$, Fig. 1b the spectrum of the catalyst obtained by depositing this porphyrin on the polyaniline support. The spectra are almost identical which indicates that the structure of porphyrin molecules is not modified by deposition. It may be thus concluded that binding of porphyrin molecules to polyaniline takes place by transfer of protons from the sulphonic acid groups $-SO_3H$ to the NH groups of polyaniline and electrostatic attraction of the porphyrin to the support (Fig. 2).

This conclusion is corroborated by the results of the UV-Vis analysis which showed that the Soret band of the supported porphyrin is identical with that observed for this porphyrin in solution.

2.1.3. Catalytic activity

The liquid phase co-oxidation of styrene and *iso*-butyric aldehyde with oxygen was carried out in the temperature range $20\text{--}35^\circ\text{C}$ and under atmospheric pressure. The static glass batch reactor, equipped with a reflux condenser and magnetic stirrer, was used. In a standard experiment, the reactor was filled with the acetonitrile solution of 2 mmole of styrene and 10^{-2} mmole of the unsupported catalyst (or such amount of supported catalysts, which contained $(2.3\text{--}7) \times 10^{-3}$ mmole of the active phase), air or oxygen was introduced and then 4 mmole of butyric aldehyde were added to start the reaction. The reagent mixture was vigorously stirred and the

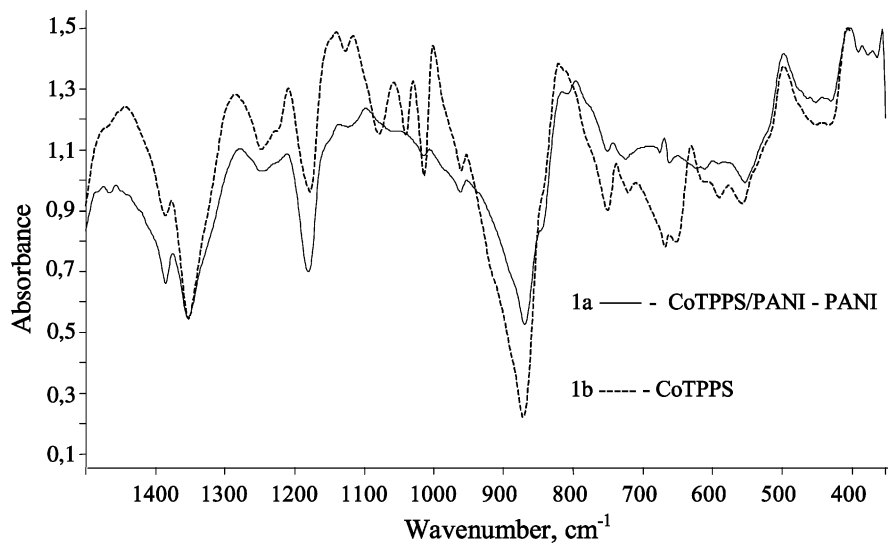


Fig. 1. IR spectrum of catalyst CoTPPS pure and on polyaniline.

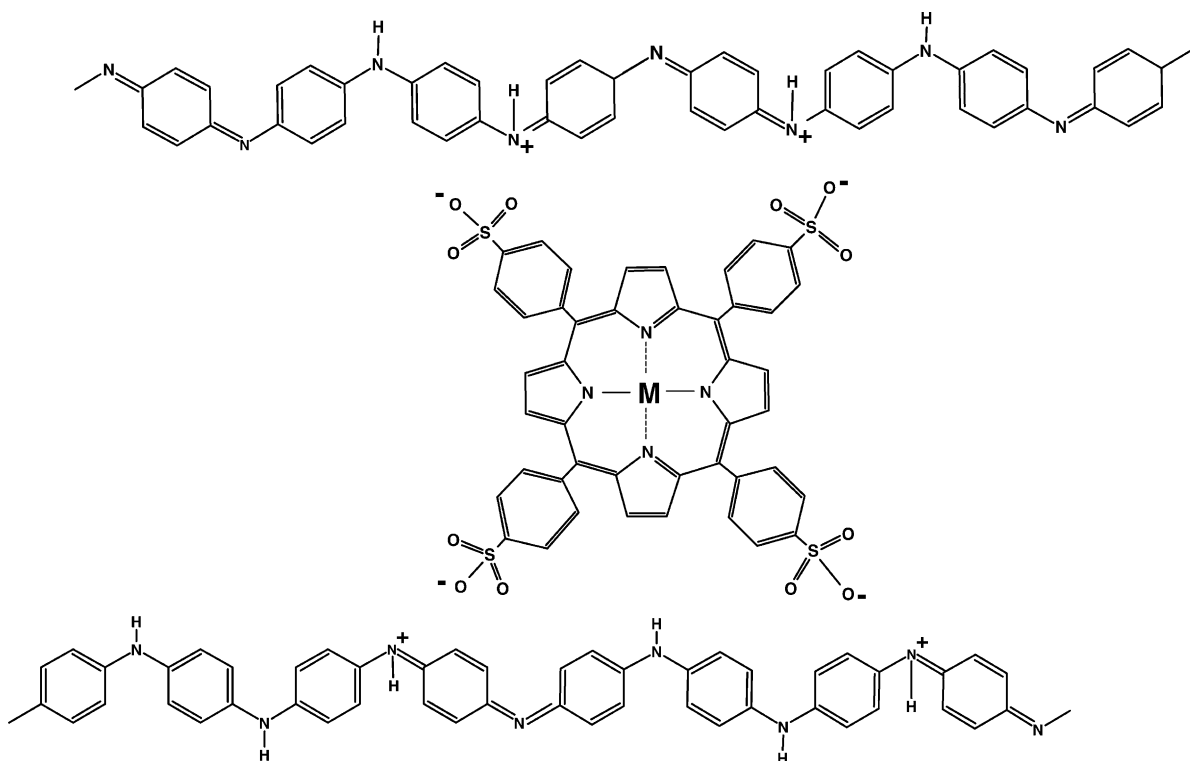


Fig. 2. Structure of tetraanionic porphyrin on polyaniline (emeraldine).

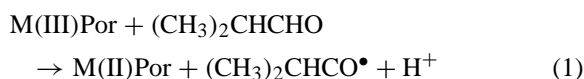
reaction was carried out for 4 h. The progress of the reaction was followed by measuring the uptake of oxygen and simultaneously small portions of the reacting mixture were withdrawn for chromatographic analysis of the conversion of styrene and *iso*-butyric aldehyde and for the determination of the amount of different products. Agilent 6890N chromatograph with FID and Carbowax 20M column was used.

In order to check the stability of the catalyst in the course of reaction an experiment was carried out in which the catalyst was washed out with acetonitrile and the liquid was checked for the catalytic activity. It turned out that the liquid shows the catalytic behaviour characteristic for the initial heterogeneous catalyst. This may be due to the fact that in the course of washing porphyrin passes into the solution together with short chains of polyaniline remaining thus heterogeneous. This indicates that the catalyst is not deactivated during the reaction.

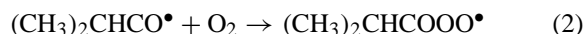
3. Results and discussion

Co-oxidation of styrene and *iso*-butyric aldehyde in the investigated conditions leads to the formation of four main products: benzaldehyde, 2-phenyloxirane (epoxystyrene) and formaldehyde, formed as the

result of the oxidation of styrene, and *iso*-butyric acid—the product of the oxidation of *iso*-butyric aldehyde. Two minor products of the oxidation of styrene: 1-phenylethanone and phenylacetaldehyde are also formed in smaller quantities. They are the result of isomerization of epoxystyrene, the epoxides being known to undergo a tautomeric hydrogen shift with the formation of acyl group. Oxidation of styrene with oxygen does not proceed without the presence of *iso*-butyric aldehyde nor without porphyrin which indicates that the chain reaction is initiated by interaction of *iso*-butyric aldehyde with the porphyrin containing trivalent metal:



The *iso*-butyric acyl radical reacts with molecular oxygen to form *iso*-butyric acylperoxy radical:



which is involved in chain propagation and finally transforms into *iso*-butyric acid.

Iso-butyric acylperoxy radical is the intermediate, responsible for the transfer of oxygen from its molecular form in the gas phase to the products of styrene oxidation. This conclusion follows from Fig. 3, in

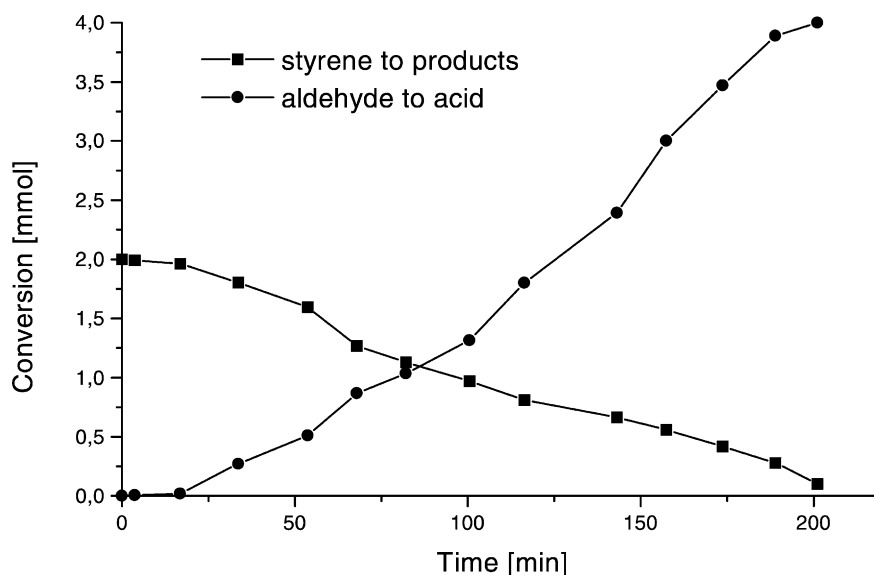
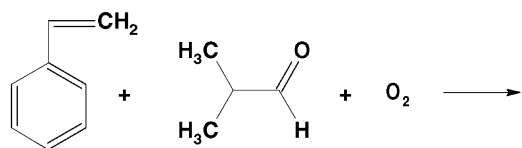
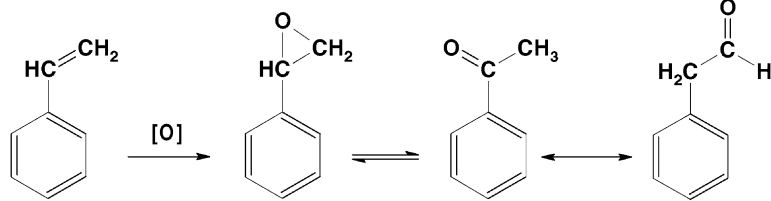


Fig. 3. Conversion of styrene and aldehyde in the reaction in the presence of CoTPPS.

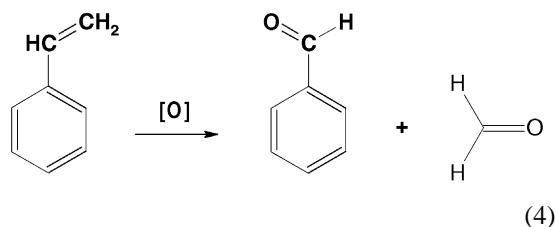
which the conversions of styrene and *iso*-butyric aldehyde, observed in their co-oxidation in the presence of CoTPPS are plotted. It may be seen that after first 100 min of the reaction the conversion of styrene is equal to the conversion of *iso*-butyric aldehyde to acid. Then, the conversion of *iso*-butyric aldehyde increases more rapidly due to the oxidation of its excess so that after the end of the reaction the ratio of the conversion of *iso*-butyric aldehyde and styrene attains the value 2, reflecting the proportion of these compounds in the initial reacting mixture. The experiment in which epoxystyrene instead of styrene was introduced in the reaction mixture with CoTPPS as catalyst showed that no formation of benzaldehyde takes place. This result indicates that benzaldehyde is not the product of a consecutive reaction of epoxystyrene, but apparently is formed in a parallel reaction directly from styrene. Thus, the process of co-oxidation of styrene and *iso*-butyric aldehyde may be described as composed of two parallel reactions [15]:



- (a) oxidation of styrene to epoxystyrene with consecutive isomerization to phenylacetaldehyde and 1-phenylethanone:

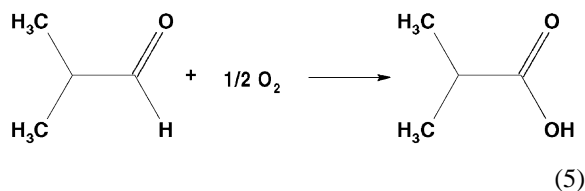


- (b) oxidation of styrene to benzaldehyde and formaldehyde:

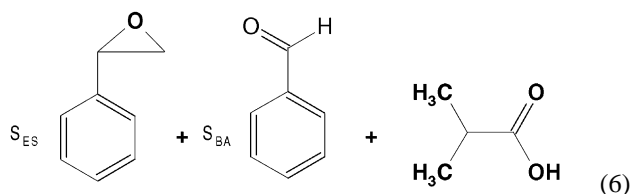


In the case of both reaction pathways the ratio styrene to *iso*-butyric aldehyde is equal to 1:1 and therefore independently of the selectivity along these pathways in the presence of the given catalyst this ratio remains 1:1 and results shown in Fig. 3 are obtained.

In the calculations of the overall stoichiometry of the reaction one should also take into account the oxidation of the excess *iso*-butyric aldehyde, present in the reaction medium, to *iso*-butyric acid:



Oxidation reactions taking place in the studied mixture can be thus described by a following overall equation:



where S_{BA} and S_{ES} represent the selectivities of the reaction to benzaldehyde and epoxystyrene, respectively.



Fig. 4 shows the amount of oxygen consumed during the reaction of co-oxidation of styrene and *iso*-butyric aldehyde, carried out in the presence of CoTPPS catalyst at 35 °C in oxygen. It is in excellent agreement with the amount calculated on the basis of Eq. (6) with the selectivity to benzaldehyde being 66.3% and that to epoxystyrene and products of its isomerization 33.7% (Fig. 5).

Results of the determination of catalytic activity of CoTPPS unsupported and supported on polyaniline

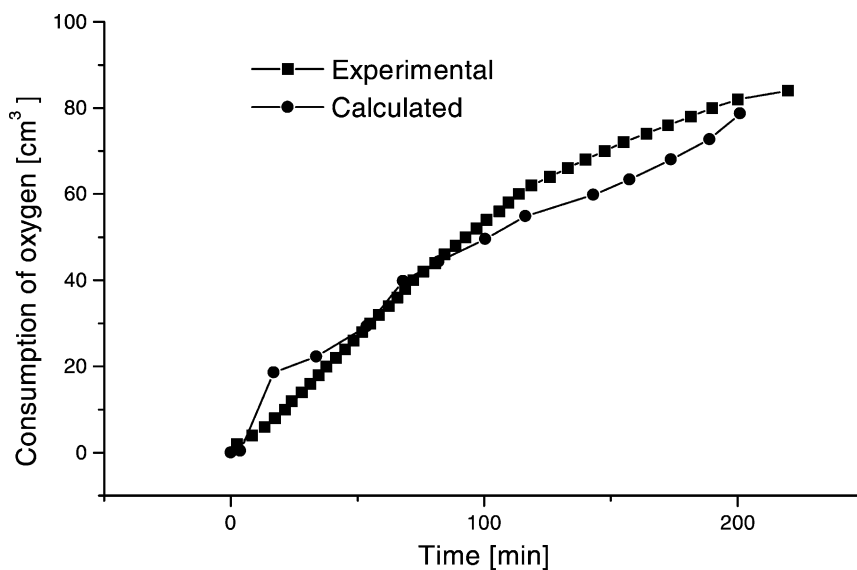


Fig. 4. Consumption of oxygen in oxidation of styrene at 35°C in the presence of unsupported CoTPPS as catalyst.

at different concentrations in co-oxidation of styrene and *iso*-butyric aldehyde with gas phase oxygen are summarized in Table 1. Reaction has been studied at temperatures 20, 30 and 35°C for 4 h and all data refer to the results of analysis of the reaction mixture

after 4 h of reaction. In the case of homogeneous liquid phase reaction in the presence of unsupported CoTPPS 100% conversion is attained after 4 h (Fig. 5) already at 20°C and the calculated TOF amounts to 57.

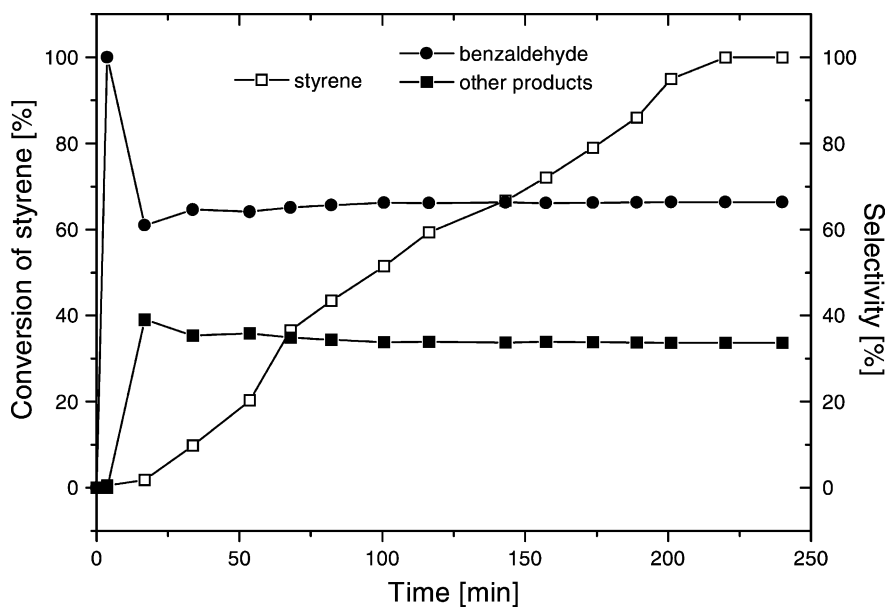


Fig. 5. Kinetics of the oxidation of styrene at 35°C and CoTPPS pure as catalyst.

Table 1
Co-oxidation of styrene and *iso*-butyraldehyde in the presence of CoTPPS as catalyst

CoTPPS	wt. %	Temperature reaction (°C)	TOF ^a	Conversion of styrene (%)	Selectivity (%)			
					Reaction products			
					Benzaldehyde	2-Phenyloxirane	Phenylacetaldehyde	1-Phenylethanol
Unsupported	–	35	57.0	100	66.3	20.6	9.6	3.5
		30	52.0	100	65.4	19.2	9.7	5.7
		20	49.0	100	60.7	17.9	14.7	6.7
	6.8	35	20.9	29.3	38.5	38.8	22.7	–
		30	18.1	25.4	29.2	58.4	12.4	–
		20	8.6	12.1	20.8	74.6	4.3	0.3
Supported on PANI	4.0	35	22.1	18.1	38.8	49.5	11.7	–
		30	14.6	12.0	43.6	41.5	14.9	–
		20	6.6	5.4	50.5	28.2	21.3	–
	2.4	35	12.4	5.7	42.2	40.3	17.5	–
		30	10.2	4.7	42.1	37.3	20.6	–
		20	5.2	2.8	50.5	25.2	24.3	–

^a mmol_{substrate}/(mmol_{cat} h).

At higher temperatures 100% conversion has been attained at shorter time, so TOF must be much higher. The reaction follows preferentially path II (Eq. (4)) to benzaldehyde with 60% selectivity and this selectivity rises slightly with increasing temperature. Consequently, the selectivity along reaction path I (Eq. (3)) to epoxystyrene and products of its isomerization decreases with temperature. After supporting CoTPPS on polyaniline the conversion drops with the decreasing concentration of CoTPPS in the catalysts (increasing number of monomers per porphyrin molecule). This is accompanied by a considerable decrease of TOF which indicates that either not all supported porphyrin molecules are accessible for

the reactants, or that activity of porphyrin molecules is modified by linking it with polyaniline. The fact that TOF increases rapidly with rising temperature seems to point to the second explanation—the modification of reactivity due to interaction with the support. Simultaneously, the change of selectivity is observed. The preferred pathway becomes now reaction path I (Eq. (3)) to epoxystyrene and product of its iso-merization phenylacetaldehyde with selectivity of 78.9% at room temperature, decreasing to 61.5% at 35 °C. It is interesting that the temperature dependence of selectivity changes with decreasing concentration of CoTPPS in polyaniline and the selectivity to epoxystyrene and phenylacetaldehyde increases

Table 2
Co-oxidation of styrene and *iso*-butyraldehyde in the presence of FeTPPS as catalyst

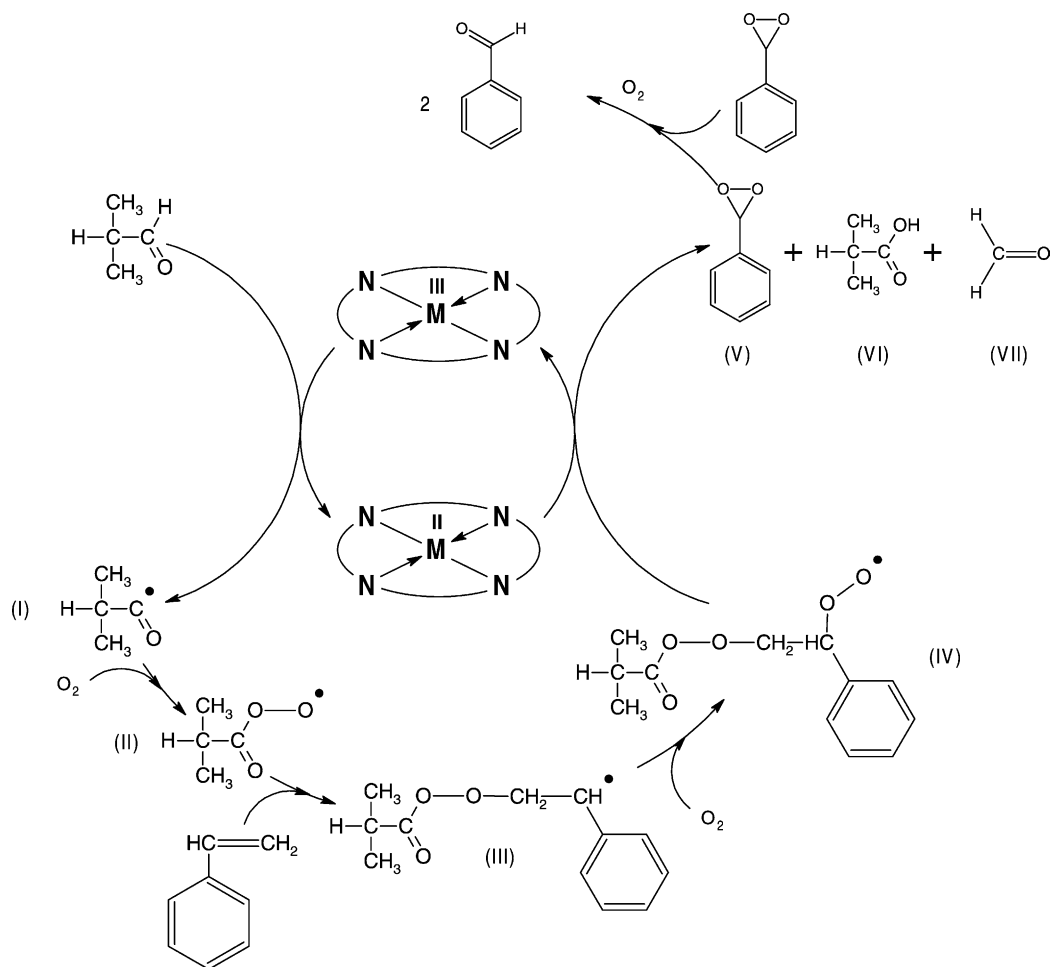
FeTPPS (wt. %)	Temperature reaction (°C)	TOF ^a	Conversion of styrene (%)	Selectivity (%)			
				Reaction products			
				Benzaldehyde	2-Phenyloxirane	Phenylacetaldehyde	1-Phenylethanol
Unsupported	35	0.9	10.1	52.2	31.4	16.4	0
	30	0.2	3.4	58.3	23.2	18.5	0
	20	0.1	0.9	72.5	20.3	7.2	0
Supported on PANI 0.36	35	4.5	0.7	64.1	22.2	13.7	0
	30	3.6	0.7	83.7	11.6	4.7	0
	20	0.7	0.1	100	0	0	0

^a mmol_{substrate}/(mmol_{cat} h).

Table 3
Co-oxidation of styrene and *iso*-butyraldehyde in the presence of MnTPPS as catalyst

MnTPPS	wt.%	Temperature reaction (°C)	TOF ^a	Conversion of styrene (%)	Selectivity (%)			
					Reaction products			
					Benzaldehyde	2-Phenyloxirane	Phenylacetaldehyde	1-Phenylethanol
Unsupported	–	20–35	0	0	0	0	0	0
Supported on PANI	8.0	35	26.0	4.9	33.8	38.8	27.4	0
		30	14.0	2.7	50.5	28.2	21.3	0
		20	1.1	0.2	100	0	0	0

^a mmol_{substrate}/(mmol_{cat} h).



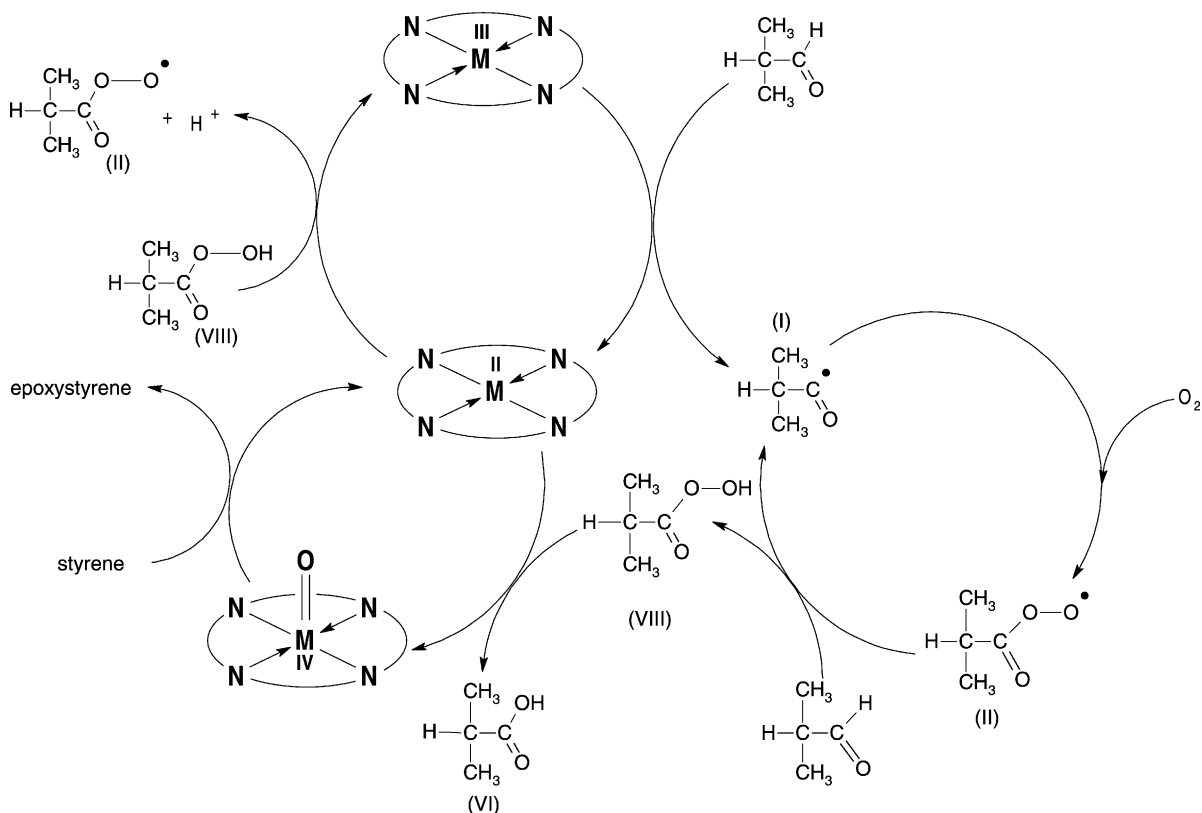
Scheme 3. The mechanism reaction pathways to benzaldehyde.

with raising the reaction temperature from 49.5% at 20 °C to 61.2% at 35 °C.

Fig. 5 shows the kinetics of the reaction as measured at 35 °C. The kinetic curves have the shape characteristic for an autocatalytic chain reaction. The fact that the shape is similar for unsupported and supported CoTPPS may be taken as an indication that the same mechanism operates in all cases. The change of selectivity in the course of this reaction for the unsupported CoTPPS is represented also in Fig. 5. It may be seen that at first benzaldehyde is formed as the only product, then after some induction time epoxystyrene appears and both products are formed in two parallel reaction pathways at practically the same rate.

Results of the studies of co-oxidation of styrene and *iso*-butyric aldehyde with gas phase oxygen in the presence of FeTPPS as catalysts are summarized in Table 2. This catalyst is about one order of magnitude less active than CoTPPS. The conversion in the homogeneous liquid phase oxidation in the presence

of unsupported FeTPPS, achieved after 4 h reaction, amounts to about 1% at 20 °C and rises to 10% at 35 °C. After supporting FeTPPS on polyaniline the conversion decreases, but TOF considerably increases, which indicates that FeTPPS becomes more active after supporting it on polyaniline. Thus, the decrease of total activity of the catalyst is due to the strongly reduced number of porphyrin molecules in the catalyst, in which their concentration was one porphyrin to 3000 monomers. Similarly as in the case of CoTPPS reaction pathway II (Eq. (4)) to benzaldehyde is preferentially followed, but supporting FeTPPS on polyaniline makes this reaction pathway even more favoured so that at 20 °C the selectivity to benzaldehyde amounts to 100%. As shown in Fig. 5 selectivity to benzaldehyde and epoxystyrene + phenylacetaldehyde remain practically unchanged during the whole reaction confirming that they are products formed along two different parallel reaction pathways.



Scheme 4. The mechanism reaction pathways to epoxystyrene.

Manganese porphyrin MnTPPS is inactive in liquid phase homogeneous co-oxidation of styrene and *iso*-butyraldehyde (Table 3). When supported on polyaniline in the concentration of 8 wt.% some activity appears. At 20 °C the conversion of 0.2% is observed with 100% selectivity to benzaldehyde. On raising temperature to 35 °C the conversion increases to 4.9% and formation of epoxystyrene and phenylacetaldehyde becomes favoured (total selectivity 66.2%) as compared to benzaldehyde.

The mechanisms of the two parallel reaction pathways to benzaldehyde and epoxystyrene may be represented by Schemes 3 and 4, respectively. Both pathways start by the interaction of *iso*-butyraldehyde with metalloporphyrin resulting in generation of *iso*-butyryl radical (I) as described by Eq. (1), which reacts with molecular oxygen to form *iso*-butyrylperoxy radical (II). The peroxy radicals are known to add easily to the double olefinic bond (Scheme 3), so a complex radical (III) is formed by addition of *iso*-butyrylperoxy radical to styrene. This complex radical reacts with a second molecule of oxygen to form another radical (IV) which picks up an electron from the porphyrin molecule and is decomposed into dioxirane (V), *iso*-butyric acid (VI) and formaldehyde (VII). Two molecules of dioxirane react with evolution of oxygen to give benzaldehyde.

The *iso*-butyrylperoxy radical (II) may also react with *iso*-butyraldehyde (Scheme 4) to form *iso*-butyryperacid (VIII) and regenerate *iso*-butylacyl radical, which propagates the chain. Peracid (VIII) reacts with reduced porphyrin decomposing into acid (VI) and forming oxidized porphyrin metal-oxo species in the case manganese and iron porphyrins or the complex with cobalt, which are known to transfer oxygen to olefins forming epoxides. In the parallel reaction the peracid may oxidize M(II)(P) into M(III)(P) generating acylperoxy radical and regenerating the catalyst. The reaction of reduced porphyrin with peracid is much more rapid than its reaction with dissolved molecular oxygen and therefore the complex Mn(II)(P)-O₂ does not play any role in the oxidation. In both reaction cycles the ratio styrene:*iso*-butyraldehyde is equal 1:1 as found experimentally.

Note that the reaction pathway leading to benzaldehyde starts directly by interaction of *iso*-butyric alde-

hyde with porphyrin, whereas the reaction pathway leading to epoxystyrene requires prior formation of oxidized porphyrin metal-oxo species. This may explain the appearance of only benzaldehyde in the very first minutes of the reaction and the initiation period in formation of epoxystyrene (Fig. 5).

4. Conclusions

The results described above permit some general conclusions to be drawn, concerning the mechanism of the co-oxidation of styrene and *iso*-butyraldehyde with gas phase oxygen in the presence of Co-, Fe- and Mn-T(*p*-SO₃H)PP in the liquid phase and supported on polyaniline:

- the reaction is proceeding along two parallel reaction pathways leading to the formation of benzaldehyde and epoxystyrene with products of its tautomeric isomerization;
- *iso*-butyraldehyde is mediating the transfer of oxygen from the gas phase to the reactants;
- the molecular ratios of both products to *iso*-butyric acid are 1:1;
- metalloporphyrin molecules are catalysts and without their presence the reaction does not occur;
- it is possible to obtain an active heterogenized porphyrin catalyst for co-oxidation of styrene and *iso*-butyraldehyde;
- the catalytic activity decreases in the order Co- >> Fe- > MnT(*p*-SO₃H)PP in the case of both porphyrins in the liquid phase and supported on polyaniline;
- supporting metalloporphyrins on polyaniline modifies their catalytic properties. Catalytic activity of Co-porphyrin decreases after supporting and the reaction pathway to epoxystyrene becomes more favoured, whereas the catalytic activity of Fe- and Mn-porphyrin increases and reaction pathway to benzaldehyde becomes dominant.

Acknowledgements

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