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Three generations of cobalt porphyrins as catalysts in oxidation of cycloalkanes

K. Pamin*[a], E. Tabor[b], S. Górecka[c], W.W. Kubiak [d], D. Rutkowska-Zbik[a], J. Połtowicz*[a]

Abstract: Three generations of cobalt porphyrins were synthesized, physicochemically characterized by FTIR and UV-Vis spectroscopy as well as cyclic voltammetry and applied as catalysts in oxidation of cycloalkanes with molecular oxygen as air under mild conditions. It was found that all the examined catalysts were active in the tested reaction and their catalytic activity varied with the nature and the quantity of substituents on porphyrin ring. It has been demonstrated that introduction of electron-withdrawing or electron-donating substituents at the porphyrin rings increases the activity of metallocomplexes. It was exhibit, for the first time, that the II generation of cobalt porphyrins in cycloalkanes oxidation show higher activity in comparison to cobalt porphyrins of III generation. Relatively lower catalytic activity of III generation cobalt porphyrins can be assigned to the saddle-shaped deformations of the porphyrin macrocycle. DFT modelling of Co porphyrins and their interactions with molecular oxygen provided motives for the observed effects. On the basis of literature data and obtained results reaction mechanism is proposed and discussed.

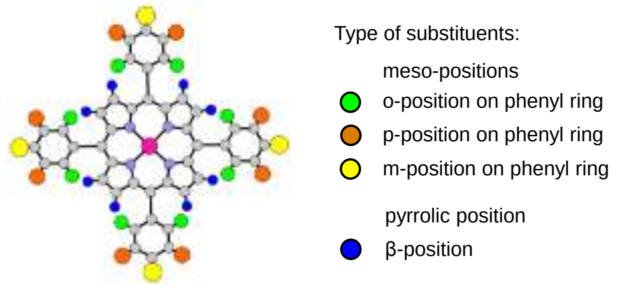
Introduction

The oxyfuntionalization of cycloalkanes into more valuable products such as alcohols and ketones is one of the most important and one of the fundamental reactions in organic synthesis[1a]. Particularly, the oxidation of cyclohexane attracts constantly much attention because cyclohexanol and cyclohexanone are important intermediates for the production of adipic acid or caprolactam. Both of them are used in the chemical industry for production of polyamids like Nylon-6,6 or Nylon-6, respectively. In the industry, the system currently in use operates with cobalt naphthenate as catalyst, molecular oxygen as air, reaction temperature in the range 155-160ºC and air pressure of 1 MPa. The conversion around 4% and selectivity of about 85% accomplished in this process means that a large stream of unreacted cyclohexane is constantly circulating in the installation for cyclohexane oxidation[1b,c]. Therefore, this makes the oxidation of cyclohexane the least efficient of all major industrial chemical processes.

The XXI century is called "the century of new materials" because only the synthesis of new materials can allow mankind to maintain the current development. It is also the century which brings a new demands for the society, such as the idea of the sustainable development which can be reached using different approaches[1d]. One of them relays on the variation of the reaction conditions in the chemical process through the introduction of a new catalysts which permits the milder reaction condition application.

The nature has chosen metalloporphyrins as active elements of enzymes and other biologically active compounds. Macrocyclic complexes like metalloporphyrins have received much attention in the field of catalytic hydrocarbon oxidation and they are good candidates for catalytic centers. They exhibit multidentate ligand systems that bind transition metal ions in the multiple oxidation states. The electronic structures of porphyrin ligands can be altered by a rational synthesis, tailoring their composition for introduction of those elements that are necessary to achieve defined properties.

The synthetic metalloporphyrins have been used extensively as biomimetic catalysts for hydroxylation of hydrocarbons, oxidation of aromatic compounds and olefins epoxidation[2a,b]. Such studies could help in the understanding of the complex biological processes involved in the enzymatic reactions with cytochrome P450[2c]. This enzyme is responsible for hydroxylation of nonpolar substrates[2d,e]. Therefore, the synthesis of porphyrins and metalloporphyrins has received the a lot of attention among scientists as highly active catalysts for hydroxylation of alkanes and epoxidation of olefins. The currently available synthetic methods allow one to synthesize porphyrin ligands carrying different substituents either at meso- or β-pyrrolic positions or both at meso- and β-pyrrolic positions (Scheme 1). Porphyrins used for the preparation of complexes with different transition metals can be divided into ligands of I, II and III generation. The I generation porphyrin has no or one substituent on the phenyl ring in porphyrin macrocycle[2d]. Lindsay synthesis[3a] permits the development of the II generation porphyrins by the introduction of more electron-withdrawing or/and electron-donating substituents at the porphyrin macrocycle.



Scheme 1. Co porphyrin with substituents on meso- and β-pyrrolic positions.

Metalloporphyrins of the II generation have been extensively studied as catalysts with different oxygen donors[3b,c]. The demand for the synthesis of porphyrin ligands with the substitution on both meso- and β-pyrrolic positions resulted in III generation porphyrins on the way of the evolution of the synthetic procedures involving the perhalogenation of the I and II generation porphyrins. Perhalogenation of porphyrin ligand was the method of choice for the formation of the increased electron deficiency of the metalloporphyrin. The enhanced catalytic

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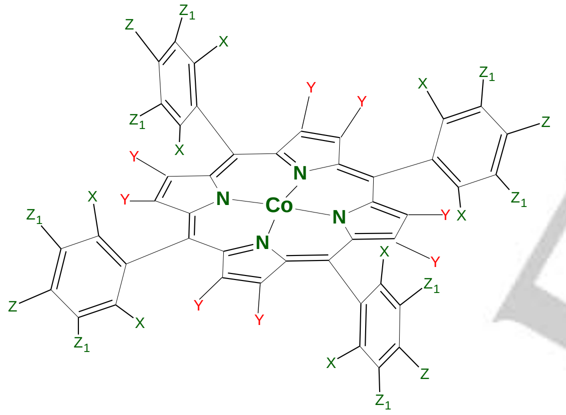
Supporting information for this article is given via a link at the end of the document.((Please delete this text if not appropriate)) activity observed for the II and III generation of porphyrins is related to the protection of macrocyclic ligand from the oxo-dimer formation and oxidative self-destruction during catalysis. The synthetic iron and manganese porphyrins are among the most studied metallocomplexes as catalysts in different oxidation processes[4a-f,2a,2f-h]. On the contrary, there are only a few examples in the literature dealing with the cobalt porphyrins catalyzed oxidation of cycloalkanes[4a-d,2a,2i].

Recently, we have described the application of both manganese and iron porphyries as well as their µ-oxo analogs with different electron-donating or electron-withdrawing substituents in the oxidation of cyclooctane to its oxygenates[5a,b]. Our investigations demonstrated that these metalloporphyrins were catalytically active in the oxidation process and their activity depend on the structure of porphyrin macrocycle. It was also found that the yield of products in hydroxylation reaction shows an almost linear relationship with the number of the halogens on the porphyrin macrocycle.

In this paper we continue our study on the catalytic activity of metalloporphyrins in the oxidation of cycloalkanes to cycloketone and cycloalcohol. We have applied as catalysts three generations of cobalt porphyrins with various electron-donating or electron-withdrawing substituents to modify their physicochemical properties and catalytic activity. Their structures are presented in Figure1. We exhibit here, for the first time, that the II generation Co porphyrins are catalytically more active than those of III generation in the oxidation of cycloalkanes with molecular oxygen.



Co porphyrin	X	Z	Z1	Y	NoS[a]
CoTPP	H	H	H	H	0
CoTTP	H	CH_3	H	H	4
CoT(p-Cl)PP	H	Cl	H	H	4
CoTDCPP	Cl	H	H	H	8
CoTMP	CH_3	CH_3	H	H	12
CoTPFPP	F	F	F	H	20
CoTDCPβN_6P	Cl	H	H	NO_2	14
CoTDCPβCl_8P	Cl	H	H	Cl	16
CoTPFPβBr_8P	F	F	F	Br	28

[a] Number of substituents.

Figure 1. Co porphyrins: I generation (blue color), II generation (orange color), III generation (green color)

Results and Discussion

Syntheses and Characterizations

UVVis Absorption Spectra

UVVis spectra of metalloporphyrins are fingerprints of their structures. Generally, metalloporphyrins possess characteristic UVVis spectra with 2 distinct regions: Soret band at about 380 – 500 nm and Q bands at 500 – 750 nm. First region includes the transition from the ground state S0 to the second excited state S2 and the resulting band is called the Soret or B band. The second region covers weak transitions from the ground state S0 to the first excited state S1 provoking the formation of rather weaker intensity Q bands. Their relative intensity is dependent on the kind and the position of substituents on the macrocyclic ring. UVVis spectra of Co porphyrins were measured as 10^{-5} solutions in dichloromethane and the results are gathered in Table 1.

Table 1. UVVis spectra of Co porphyrins.

Catalyst	Soret band [nm]	Q bands [nm]
TPP	417	514 538 585 620
CoTPP	410	528
CoTTP	412	529
CoT(p-Cl)PP	411	529
CoTMP	412	529
CoTDCPP	410	531 560
CoTPFPP	404	526 554
CoTDCPβN_6P	446	546
CoTDCPβCl_8P	436	556 585
CoTPFPβBr_8P	442	558 588

In Table 1, the positions of Soret band for TPP ligand and series of Co porphyrins as well as one to four characteristic bands in the visible region are listed. Insertion of cobalt atom and different substituents into the porphyrin ring influences both the position of Soret band and the intensity and number of Q bands. The largest variations in Soret band locations are observed for substituents in β-pyrollic positions (Scheme 1). Moreover, introduction of cobalt results, for porphyrins of I and II generation, in blue shift of Soret band. However, for III generation Co porphyrins with substituents in β-pyrollic and meso-positions Soret band is red-shifted. For example, the introduction of electron-withdrawing groups like NO_2 or Cl into CoTDCPP induces the change of Soret band position from 410 nm to 446 nm for NO_2 or 436 nm for Cl substituents. Similarly, in the case of CoTPFPP, the incorporation of Br groups renders the Soret band red shift from 404 nm for CoTPFPP to 442 nm for CoTPFPβBr_8P.

Cyclic Voltammetry Measurements

Redox properties of Co porphyrins were studied using cyclic voltammetry, which is reliable method to asses oxidation skills of studied catalysts. Table 2 presents the results of the voltammetric measurements for the series of Co porphyrins. All the studied Co porphyrins undergoes one-electron oxidation processes. Oxidation of unsubstituted CoTPP porphyrin, treated here as reference sample, occurs at 280 mV. However, the introduction of substituents on the porphyrin ring modifies oxidation potential. For example, the addition of electron-withdrawing groups either to meso- or to β-pyrollic positions on the porphyrin macrocycle induces easier reduction and more difficult oxidation. By contrast, in the presence of electron-donating groups on Co porphyrin reduction is harder while oxidation proceeds more readily.

Table 2. Cyclic voltammograms of Co porphyrin catalysts

Co porphyrin	Potential E$_{OX}$, [mV]	Number of substituents	Co porphyrin generation
CoTMP	271	4	I
CoTTP	278	12	II
CoTPP	280	-	I
CoT(p-Cl)PP	282	4	I
CoTDCPP	292	8	II
CoTPFPP	295	20	II
CoTDCPβN$_6$P	290	14	III
CoTDCPβCl$_8$P	290	16	III
CoTPFPβBr$_8$P	308	28	III

The presence of electron-withdrawing groups reduces the electron density on the metal atom. On the other hand, electron-donating substituents act in quite the opposite way, rendering the increase of electron density in the vicinity of metal atom.

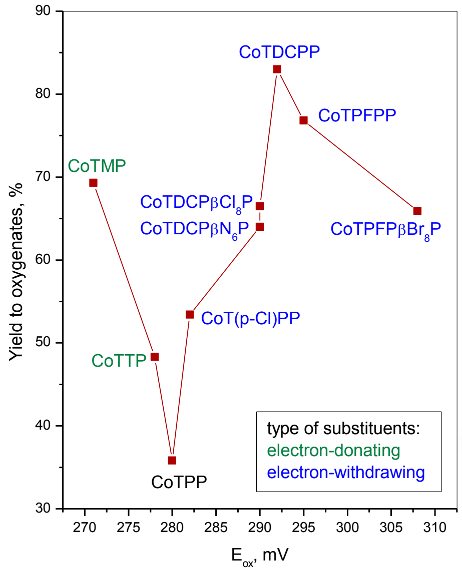
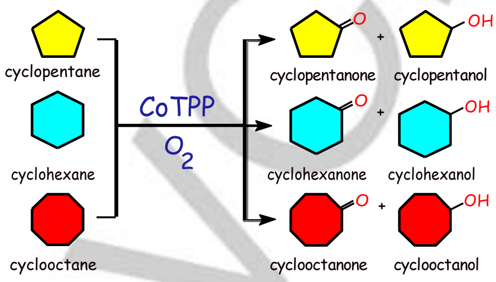


Figure 2. Catalytic activity of cobalt porphyrins with different substituents as a function of their oxidation potentials. The yield is based on molecular oxygen in the reaction vessel.

Introduction of electron-donating substituents on the porphyrin macrocycle (CoTTP and CoTMP) renders the decrease of their oxidation potentials. On the contrary, oxidation potential of cobalt porphyrins grows upon the addition of electron-withdrawing groups and generally is higher than the one established for CoTPP. Figure 2 depicts the relationship between the yield to oxygenates and the oxidation potential of the Co porphyrins. The presence of both, the electron-donating and the electron-withdrawing substituents on porphyrin ring improves the catalytic activity in comparison with unsubstituted CoTPP. In particular, for electron-donating groups on porphyrin ring, with the decrease of oxidation potential E$_{ox}$ the yield to oxygenates grows. In the presence of electron-withdrawing substituents the increase of the E$_{ox}$ is accompanied by the rise of the yield to oxygenates. These results are in line with findings reported by Guo[6] for iron μ-oxo porphyrins in the cyclohexane hydroxylation with iodosobenzene as oxygen donor. Our previous studies, which were performed in the presence of manganese[5a] or iron[5b] porphyrins bearing electron-donating or electron-withdrawing groups, also confirm catalytic performance of Co porphyrins in the oxidation of cyclooctane by molecular oxygen.

Catalytic results

Three members of homologous series, namely cyclopentane, cyclohexane or cyclooctane were applied as substrates and studied in oxidation catalyzed by cobalt porphyrin complex CoTPP (Scheme 2).



Scheme 2. Cycloalkanes oxidation.

The main products of cycloalkane oxidation with molecular oxygen are cycloketone and cycloalcohol (Scheme 2). Blank test of liquid phase oxidation of cyclooalkane carried out in the absence of a catalyst showed lack of oxygenates in the reaction conditions. For cyclopentane oxidation, in the presence of CoTPP, after 6 h of reaction only 3.8% yield to ketone and 1.2% yield to alcohol were obtained (Figure 3).

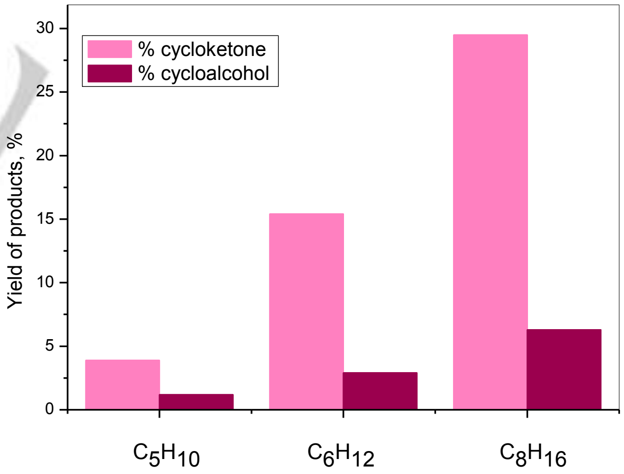


Figure 3. Oxidation of C5, C6 and C8 cycloalkanes by unsubstituted CoTPP.

The oxidation of cyclohexane resulted in 15.4% yield to cyclohexanone and 2.9% yield to cyclohexanol. In the similar reaction conditions, cyclooctane was converted to cyclooctanone and cyclooctanol with yields of 29.5% and 6.3%, respectively.

Taking into account the above results the following order of catalytic activity in the studied reaction was established: cyclooctane > cyclohexane > cyclopentane, and hence cyclooctane was finally selected for further investigations.

It is well-known that the selective catalytic oxidation of C-H bonds results in the formation of hydroperoxides[7]. However, iodometric titration of reaction mixture, analysed after 6 h of the reaction, enables the evaluation of the amount of cyclooctane hydroperoxide as 0.06%, which is too low to have any impact on the results of the further GC analysis. Hydroperoxide once formed upon the action of the catalyst in the course of the reaction transforms to alcohol and ketone. In our reaction conditions cycloalkyl hydroperoxide in the presence of cobalt porphyrin catalysts almost completely decomposes.

In this paper we report the effect of the Co porphyrin ring structure of the series of three generations cobalt porphyrins on their catalytic activity in the oxidation of cyclooctane with molecular oxygen. The main products of the studied reaction are cyclooctanone and cyclooctanol. The formation of secondary oxidized products such as 1,5-cyclooctanedione and 1,4-cyclooctandione was not confirmed by GC analysis. As catalysts the unsubstituted cobalt porphyrins or Co porphyrins with one substituent at the phenyl ring (I generation), those bearing more substituents at the phenyl rings (II generation) and cobalt porphyrins with groups both at the phenyl and pyrrole rings (III generation) were applied. The results summarized in Figure 4 clearly show that all the examined macrocyclic catalysts were active in the studied reaction and their catalytic activity varied with the nature and the quantity of substituents at the porphyrin ring.

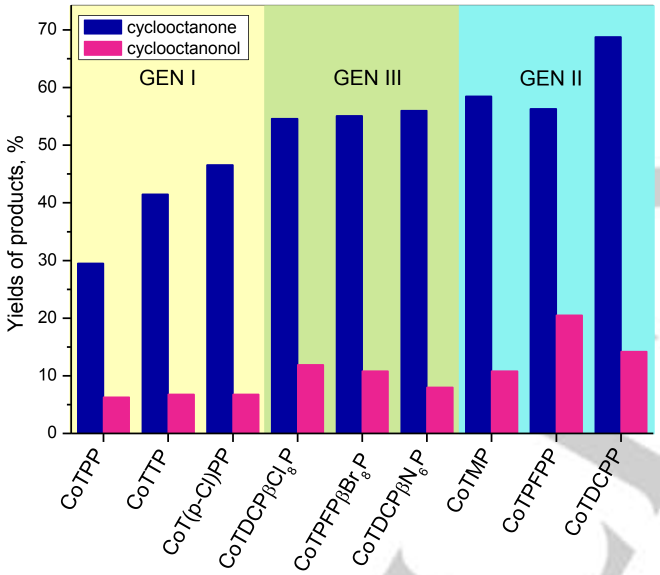
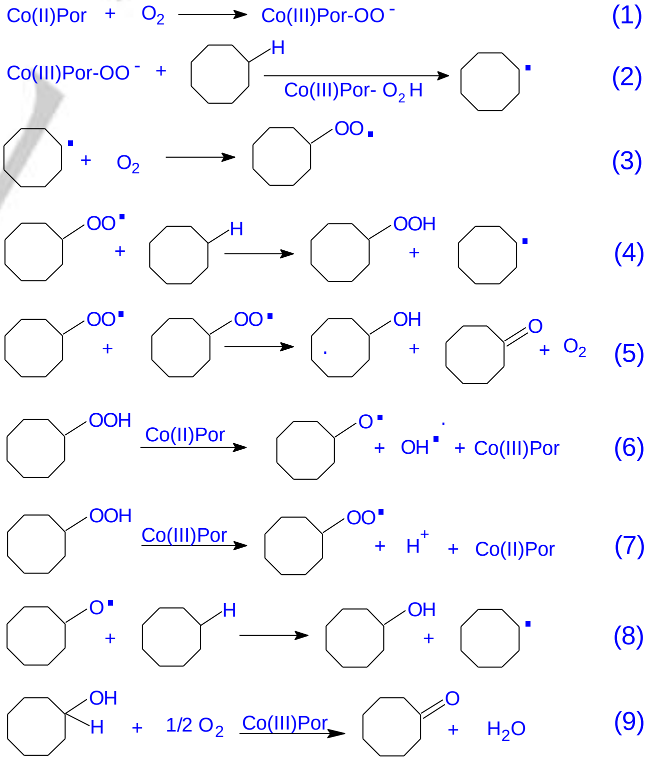


Figure 4. Cyclooctane oxidation in the presence of Co porphyrins. The yields are based on molecular oxygen in the reaction vessel.

As one can see catalysts can be divided into three groups, depending on the porphyrin generation. In the case of I generation metalloporphyrins, the lowest catalytic activity in cyclooctane oxidation is observed for unsubstituted CoTPP. CoTTP complex with four electron-donating groups (CH$_3$) demonstrates significant increase of yield to cyclooctanone (41.5%). And the last complex in this group of catalysts, CoT(p-Cl)PP, belonging to the I generation metalloporphyrins with four electron-withdrawing groups (Cl) shows further rise of cyclooctanone yield. At the same time yield to cyclooctanol remains almost stable for all three I generation metalloporphyrins. III generation Co porphyrins, namely CoTDCPβCl$_8$P, CoTPFPβBr$_8$P and CoTDCPβN$_6$P, exhibit continued growth of both, the yield to cyclooctanone and to cyclooctanol. However, relatively moderate catalytic activity of these considerably substituted Co porphyrins is rather surprising since it has been repeatedly demonstrated that introduction of electron-withdrawing or electron-donating substituents at the porphyrin rings increases the activity of metallocomplexes[8a]. And finally, the highest catalytic activity can be observed for the catalysts pertaining to the group of II generation Co porphyrins. CoTMP complex with twelve CH$_3$ groups demonstrates slightly higher yield to cyclooctanone (58.5%), however the yield to cycloalcohol is comparable with the results observed for III generation of Co porphyrins. Although CoTMP complex possesses exclusively electron-donating substituents its high catalytic performance in the studied reaction is not surprising. Similar metalloporphyrins, MnTMP and FeTMP, have been widely applied and they demonstrated superior catalytic activity in oxidation processes[4a,8b-c]. For CoTPFPP with 20 fluorine substituents the yield to cyclooctanone slightly diminishes (56.3%) but on the other hand this catalyst is the most active in the formation of cyclooctanol. CoTDCPP porphyrin having 8 Cl groups in phenyl rings is the most active among all the studied catalysts in the oxidation of cyclooctane yielding 68.8% of cyclooctanone and 14.2% of cyclooctanol. Summing up, it is worth notice that II generation Co porphyrins are more catalytically active than those of III generation. Entirely similar phenomenon was described by Meunier et al.[8d] who showed that Mn porphyrins of II generation (MnTDCPP) are more catalytically active than those of III generation (MnTMβBr$_8$P) in the cyclohexane hydroxylation by KHSO$_5$. Moreover, it was also demonstrated that III generation MnTDCPβCl$_8$P is less active than II generation MnTDCPP in the olefins epoxidation with hypochlorite[8e]. We postulate that the motive for the reverse order of catalytic activity in cyclooctane oxidation is spatial deformation of porphyrin ring structure from planar to saddle-shape.

Basing on the literature[9] and our investigations the following mechanism of oxidation with Co porphyrins as catalysts was proposed. According to the literature data[9a,10] we propose the radical chain reaction mechanism.



Scheme 3. Cycloalkanes oxidation in the presence of Co porphyrins – the mechanism

Scheme 3 presents set of reactions where the main reaction products are cycloctanone, cyclooctanol and traces of cyclohydroperoxide. Reaction starts with the activation of molecular oxygen by Co porphyrin which leads to the formation of superoxide (1) species. In the next step the latter abstracts hydrogen from cycloalkane forming the cycloalkyl radical $R^{\bullet}$ (2) and promoting the initiation of radical chain reaction[9c,11a,b]. Chain propagation step begins with the reaction of cycloalkyl radical $R^{\bullet}$ and molecular oxygen to cycloperoxyl radical $ROO^{\bullet}$ (3). Cycloperoxyl radical $ROO^{\bullet}$ may further react with the next molecule of cycloalkane producing cycloalkyl hydroperoxide ROOH and cycloalkyl radical $R^{\bullet}$ (4). In the fifth step cycloketone and cycloalcohol appear as a result of the recombination of cycloperoxyl radicals $ROO^{\bullet}$ establishing at the same time chain termination step. Cycloalkyl hydroperoxide ROOH in the presence Co porphyrin decomposes both, in the homolytic[9a,11c] or heterolytic[9a,11d] manner. In the homolytic decomposition cycloalkoxyl radical $RO^{\bullet}$ and hydroxyl radical $OH^{\bullet}$ are produced (6). On the other hand heterolytic decomposition results in the formation of cycloperoxyl radical $ROO^{\bullet}$ (7). Additional source of cycloalcohol is the reaction of cycloalkoxyl radical $RO^{\bullet}$, produced in (6), with cycloalkane molecule (8). Cycloalcohol arising in the previous steps may also be converted to cycloketone in the presence of the catalyst (9). Perhaps step (9) is the main reason for the high yield of cycloketone and only limited formation of cycloalcohol observed in our catalytic system. In contrast to our catalytic studies on cycloalkanes it is worth to recall that for oxidation of linear and branched alkanes in the presence of cytochrome P-450 the main reaction product is always cycloalcohol[11e].

DFT calculations

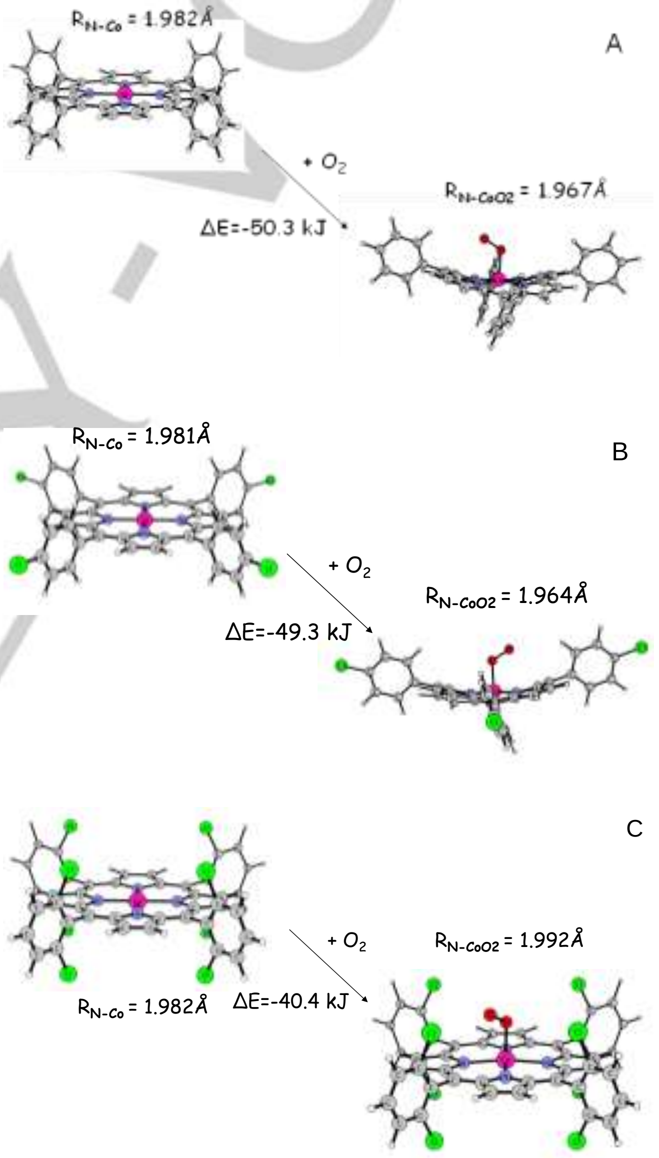
DFT modelling was employed to elucidate the dependency between catalytic properties of the Co porphyrins observed in the cycloalkanes oxidation with molecular oxygen and the spatial geometry of the studied structures. Table 3 gathers the results of the DFT calculations for the series of Co porphyrins. Doublet ground state of all the studied cobalt porphyrins with or without bound molecular oxygen molecule is found in agreement with earlier theoretical studies of similar complexes[12a,b]. The molecular oxygen is always bound in an end-on mode.

Table 3. Selected results of the DFT calculations.

Catalyst	N-Co[a] [Å]	Co-O_2[b] [Å]	q(O_2)[c]	ΔE_{O2}[d] [kJ/mol]	N-CoO_2[e] [Å]
CoTMP	1.980	1.867	-0.22	-47.1	1.991
CoTTP	1.982	1.870	-0.19	-47.0	1.993
CoTPP	1.982	1.870	-0.16	-50.3	1.967
CoT(p-Cl)PP	1.981	1.872	-0.15	-49.3	1.964
CoTDCPP	1.982	1.878	-0.11	-40.4	1.992
CoTPFPP	1.981	1.884	-0.15	-38.5	1.992
CoTDCPβN_6P	1.934	1.917	-0.08	-29.3	1.954
CoTDCPβCl_8P	1.935	1.897	-0.10	-44.0	1.956
CoTPFPβBr_8P	1.926	1.903	-0.14	-33.1	1.947

[a] average N-Co bond length. [b] atom bond length between Co and O_2. [c] total ESP charge on O_2. [d] binding energy of O_2. [e] average N-Co bond length after binding O_2.

Examination of the structures geometry for all the studied systems reveals the differences among the three generations of Co porphyrins (see Supplementary Information for Co porphyrin structures). Co porphyrins of I generation show planar structure of macrocyclic ring (Figures 5A and 5B), generation II complexes are only slightly ruffled (Figure 5C), while those of III generation exhibit saddle deformation (Figure 5D). Their distinct geometry is also reflected by the average Co-N bond lengths: in the four-coordinated complexes they are equal ca. 1.98 Å for generation I and II complexes, but are diminished to ca. 1.93 Å in the case of generation III catalysts due to their saddle deformation. Upon molecular oxygen binding to the cobalt ion the average Co-N distances (N-CoO_2) are slightly elongated in the most of the studied systems except for CoTPP-O_2 and CoT(p-Cl)PP-O_2. This indicates that the molecular oxygen molecule pulls out Co ion from the macrocycle plane in most of the cases.



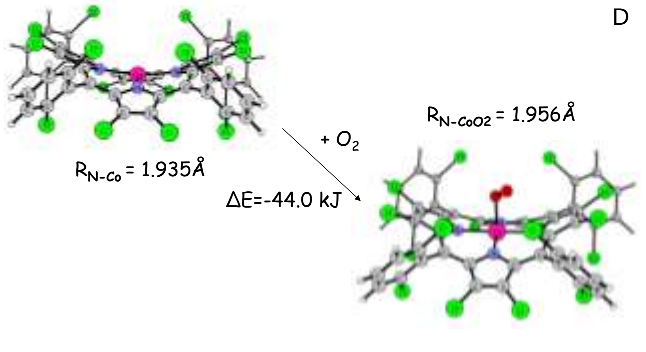


Figure 5. DFT calculations for unsubstituted CoTPP (A), CoT(p-Cl)PP with 4Cl substituents (B), CoTDCPP with 8 Cl substituents (C) and CoTDCPPβCl_8P with 16 Cl substituents (D) and upon binding O_2.

The distortions from the planarity found for the III generation Co porphyrins seems to be large enough to constitute steric hindrances in the process of O_2 binding to cobalt ion. This can be seen confronting the Co-O_2 bond lengths which are longer for the III generation in comparison to the I and II generation. Co-O_2 bond lengths of Co porphyrins with electron-donating substituents are shortened in comparison with CoTPP catalyst treated here as a reference. However, in the presence of electron-withdrawing groups Co-O_2 bond lengths become longer, comparing with CoTPP.

In general, this effect is reflected by the molecular oxygen binding energies. Figure 6 exhibits a linear correlation between Co-O_2 bond length and the molecular oxygen binding energies ΔE_{O2}, similar as shown in[12a].

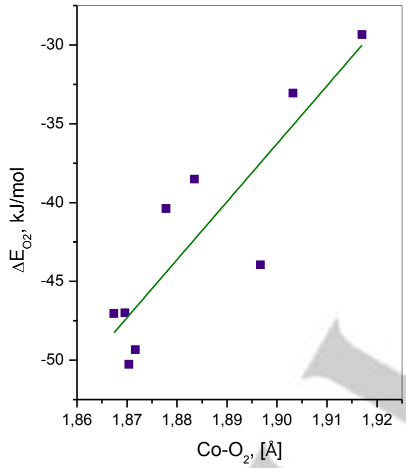


Figure 6. Linear correlation (R^2 = 0.78) between Co-O_2 bond length and dioxygen binding energies ΔE_{O2}.

Finally, the negative charge accumulated on molecular oxygen ligand (q(O_2)) indicates that it is bound in the O_2^- form, thus implying its nucleophilic character. The negative charge is located mostly on the outer oxygen atom, exposing it towards the incoming organic substrate. The O_2 ligand is more nucleophilic in the systems with electron donating-substituents (CoTTP-O_2, CoTMP-O_2). The presence of electron-withdrawing substituents leads to the smaller negative charge on O_2 as compared to the reference CoTPP-O_2 complex. Charges on O_2 confirm donor or acceptor character of substituents increasing or reducing their values referring to the unsubstituted CoTPP.

Conclusions

All the synthesized cobalt porphyrin catalysts are catalytically active in the oxidation of cycloalkanes with molecular oxygen. Their catalytic performance depends on the nature and number of substituents introduced into meso-aryl and β-pyrrolic positions of porphyrin macrocycle. It was shown that not only electron-withdrawing but also electron-donating substituents on porphyrin rings significantly improve the catalytic activity towards the formation of reaction products. It is noteworthy that II generation of cobalt porphyrins is more active than III generation. Relatively lower catalytic activity of III generation cobalt porphyrins can be assigned to the saddle-shaped deformations of the porphyrin macrocycle. DFT modelling of Co porphyrins and their interactions with molecular oxygen provided motives for the observed effects. The yield to oxygenates grows for Co porphyrins substituted with electron-donating groups on porphyrin ring with the decrease of oxidation potential E_{ox}. In the presence of electron-withdrawing substituents the increase of the E_{ox} is accompanied by the rise of the yield to oxygenates. Basing on the literature data and our investigations the oxidation mechanism of cycloalkanes by cobalt porphyrins is proposed.

Experimental Section

General

All the reagents used in this work were purchased and used directly without further purification. The I generation porphyrins TPP, TTP and T(p-Cl)PP were synthesized by condensation of pyrrole and appropriate aldehyde according to the Rothemund and Menotti procedure[2d,e]. Two steps Lindsay procedure[3a] involving acid-catalyzed condensation of pyrrole with the appropriate aldehyde into porphyrinogen, followed by its oxidation with quinone to porphyrin ligand was applied to obtain II generation porphyrin ligands TDCPP and TPFPP. Porphyrin ligand TMP was acquired using modified Lindsay method[13a]. The preparation of III generation porphyrin TDCPPβCl_8P was accomplished by the chlorination of ZnTDCPP with Cl_2 followed by the in situ removal of Zn with HCl[13b]. Ligand TPFPPβBr_8P was prepared by halogenation of NiTPFPP with Br_2 and the in situ removal of Ni with HCl[13b]. Porphyrin ligand TDCPPβN_6P was synthesized using Mansuy-Battioni method[13c] consisting in the reaction of porphyrin ligand TDCPP with fuming acid HNO_3. All the synthesized porphyrin ligands were metalated by condensation of porphyrin with cobalt acetate according to the Adler procedure[13d].

UV-Vis measurements were carried out on a Perkin Elmer Lambda 35 double beam spectrophotometer, using quartz cells of 1 cm optical path. Cyclic voltammograms were recorded in a three-electrode cell using Co porphyrin modified working electrode, platinum coil as auxiliary electrode and Ag/AgCl as reference electrode. Co porphyrin solid sample was homogenized with graphite powder and Nujol to form thick paste which was then packed into the electrode well. Cobalt porphyrins were analyzed in acetic buffer of pH=5 as electrolyte, with the scan rate of 25 mV/s. Prior to the measurements the solution was de-aerated with argon to keep air-free atmosphere over the solution during the measurement.

Catalytic reaction

The catalytic oxidation of cyclooctane (cyclopentane or cyclohexane) which simultaneously played the role of the reaction medium was performed in 1L stainless steel batch reactor at the optimum temperature of 120ºC, under the air pressure of 10 atm and with the molar ratio of cycloalkane to oxygen set at 6.5. In the typical experiment, cobalt porphyrin having the concentration of $3.3 \cdot 10^{-4}$ M was introduced into the 60 mL of substrate and the reaction was started when the required reaction conditions were attained. After 6 h of reaction time, the oxidation was stopped by immersing the hot reactor in a cold water bath and the reaction mixture was analyzed by means of Agilent Technologies 6890 N gas chromatograph equipped with a FID detector and Innowax (30 m) capillary column. The percentage yield of oxygenates (calculated as the amount of desired product obtained divided by the theoretical yield predicted by the reaction stoichiometry) was determined in the presence of chlorobenzene as internal standard. The conversion and yield of products were calculated on the basis of oxygen quantity in batch reactor.

Computational Details

The structures of the investigated porphyrins with and without attached oxygen molecule were obtained by Density Functional Theory (DFT) calculations within non-local Becke-Perdew functional[14a-e]. The Resolution-of-identity (RI) algorithm was applied in order to accelerate computation[14f-g]. The calculation consisted of geometry optimization of the studied structures with def2-SVP basis set, further confirmed with vibrational analysis. Larger basis set of def2-TZVP quality was used[14h] to compute the electronic structure and properties of the investigated system, including ESP atomic charges calculated within Merz-Kollman scheme[14i]. The present results were obtained with Turbomole v. 7.1[14j]. The reported molecular oxygen binding energies (E_b^{O2}) were computed using the following formula:

$E_b^{O2} = E_{tot}(Porf\text{-}O_2) - E_{tot}(Porf) - E_{tot}(O_2)$

where:

$E_{tot}(Porf\text{-}O_2)$ – total electronic energy of the porphyrin complex with molecular oxygen,

$E_{tot}(Porf)$ – total electronic energy of the porphyrin species,

$E_{tot}(O_2)$ – total electronic energy of the oxygen molecule.

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Keywords: cobalt porphyrin • cycloalkanes oxidation • DTF calculations • molecular oxygen • sustainability

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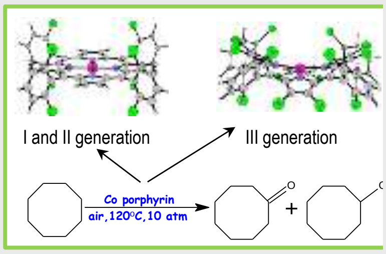

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