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# Catalytic Activity of Tetraarylporphyrins in the Oxidation Reactions of Saturated Hydrocarbons[1]

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**Abstract**—The oxidation of cyclic hydrocarbons by potassium peroxymonosulfate catalyzed by the iron and manganese complexes of tetra-(4-*N*-butylpyridinium)porphyrin, tetraphenylporphyrin, and mixed porphyrins containing phenyl and butylpyridyl substituents was studied in an aqueous acetonitrile medium. The test catalysts were dissolved in the reaction medium or adsorbed on layered aluminosilicates. It was found that the immobilization of metal complexes on layered aluminosilicates, as well as the bromination of porphyrins, decreased the activity of catalysts in a number of cases, although it improved their stability. The addition of pyridine in an equimolar amount with respect to metal complexes to the reaction mixture increased the activity of dissolved manganese complexes. An increase in the number of butylpyridyl *meso*-substituents in a porphyrin molecule improved the catalytic activity of a metal complex.

It is well known that enzymes from the cytochrome P-450 series catalyze a wide range of hydrocarbon oxidation reactions under naturally occurring conditions. The high efficiency of enzyme systems and good potential for using enzyme-catalyzed functionalization processes resulted in the appearance of a new field of science. Breslow [1] named this field biomimetics, that is, the science that studies and simulates processes and reactions occurring in living organisms under the effect of enzymes.

Among catalysts that are promising for the functionalization of saturated hydrocarbons, the metal complexes of synthetic porphyrins, which are analogs of natural cytochrome P-450, occupy a highly important place. Like natural catalysts, though to a lesser degree, these catalysts provide the selective oxidation of saturated hydrocarbons under mild conditions by using readily available environmentally benign oxidants [2].

The main disadvantage of such catalysts is their relatively low stability because a porphyrin ligand undergoes intense degradation in the course of reaction.

It is well known that the following main procedures can be used for improving the stability of metal porphyrins:

(1) The introduction of aryl substituents with bulky groups at the 2- and 5-positions into the *meso*-positions of a porphyrin ring [3];

(2) The substitution of halogen atoms or other electronegative groups for hydrogen atoms at the β-positions of a macrocyclic porphyrin ring [4];

(3) The immobilization of active metal complexes on a solid substrate [5].

In this work, we studied the effect of the above factors on the oxidation of cyclic hydrocarbons by potassium peroxymonosulfate catalyzed by the iron and manganese complexes of porphyrins.

The use of layered aluminosilicates like bentonites and montmorillonites as supports is of special interest. As distinct from polymer supports, they are not prone to oxidation. The regular structure of mineral layers suggests the possibility of catalyst intercalation into the interlamellar space and the specific orientation of a substrate in the course of an elementary act of oxidation. Therefore, these compounds were chosen as catalyst supports.

## EXPERIMENTAL

Table 1 summarizes the test porphyrins and their metal complexes. The synthesis of a mixture of phenylpyridylporphyrins was performed according to the published procedure [6]. Individual compounds **3**, **4**, and **5** were isolated from the reaction mixture by repeated chromatographic separation on silica gel. The elution was performed using a mixture of chloroform and methanol with a gradually increased fraction of the more polar component.

Target metal porphyrins **10** and **11** were prepared from porphyrins **4** and **5** by alkylation with butyl bromide. Next, they were converted into metal complexes with iron and manganese according to published procedures [7].

Complete bromination of tetrapyridylporphyrin derivatives has not been previously described in the literature. Attempts to perform this bromination similarly

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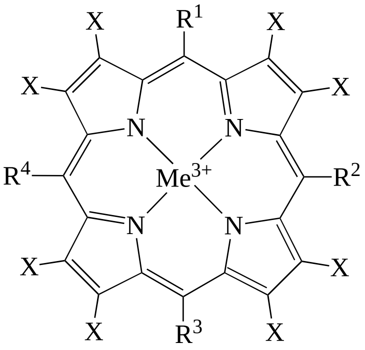
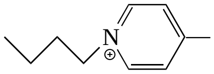
**Table 1.** Structure of the test porphyrins and metal porphyrins

| | $R^1$ | $R^2$ | $R^3$ | $R^4$ | Me | X | | Compound |
|---|---|---|---|---|---|---|---|---|
|  | *n*-BuPy | *n*-BuPy | *n*-BuPy | *n*-BuPy | Fe | H | **1** | Tetra-(4-*N*-butylpyridinium)porphyrin iron pentaperchlorate |
| | *n*-BuPy | *n*-BuPy | *n*-BuPy | *n*-BuPy | Mn | H | **2** | Tetra-(4-*N*-butylpyridinium)porphyrin manganese pentaperchlorate |
| | Ph | Ph | Ph | Ph | 2H | H | **3** | Tetraphenylporphyrin |
| | Ph | Ph | Ph | Py | 2H | H | **4** | Triphenyl-α-monopyridylporphyrin |
| | Ph | Ph | Py | Py | 2H | H | **5** | α,γ-Diphenyl-β,δ-dipyridylporphyrin |
| | *n*-BuPy | *n*-BuPy | *n*-BuPy | *n*-BuPy | Fe | Br | **6** | Tetra-(4-*N*-butylpyridinium)octabromoporphyrin iron pentaperchlorate |
| | *n*-BuPy | *n*-BuPy | *n*-BuPy | *n*-BuPy | Mn | Br | **7** | Tetra-(4-*N*-butylpyridinium)porphyrin zinc tetraperchlorate |
| | *n*-BuPy | *n*-BuPy | *n*-BuPy | *n*-BuPy | Zn | H | **8** | Tetra-(4-*N*-butylpyridinium)porphyrin zinc tetraperchlorate |
| | *n*-BuPy | *n*-BuPy | *n*-BuPy | *n*-BuPy | 2H | Br | **9** | Tetra-(4-*N*-butylpyridinium)octabromoporphyrin tetraperchlorate |
| | Ph | Ph | Ph | *n*-BuPy | Mn | H | **10** | Triphenyl-(4-*N*-butylpyridinium)porphyrin manganese diperchlorate |
| | Ph | Ph | *n*-BuPy | *n*-BuPy | Mn | H | **11** | Diphenyl-di-α,γ-(4-*N*-butylpyridinium)porphyrin manganese triperchlorate |
| | Ph | Ph | Ph | Ph | Mn | H | **12** | Tetraphenylporphyrin manganese perchlorate |

Note:  = *n*-BuPy.

to the reactions of other tetraarylporphyrins, that is, by long-term treatment with *N*-bromosuccinimide, were unsuccessful. In this case, no more than six bromine atoms were inserted at the β-positions of a macrocyclic ring. In this work, we developed a procedure for the bromination of tetrapyridylporphyrin and related phenylpyridylporphyrins to the highest degree. For this purpose, the zinc complexes of alkylpyridiniumporphyrins were treated with bromine in an amount somewhat higher than equimolar.

The 5,10,15,20-tetra-(4-*N*-butylpyridinium)porphyrin zinc tetraperchlorate complex (**8**) was prepared in accordance with the published procedure [8].

For the synthesis of 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetra-(4-*N*-butylpyridinium)porphyrin tetraperchlorate (**9**), zinc complex **8** (110 mg; 0.085 mmol) was dissolved in 200 ml of a mixture of methanol and 1.5 ml of pyridine. The solution was brought to a boil, and a solution of 0.5 ml of bromine (19.4 mmol) in 25 ml of methanol was added with intense stirring for 4 h. The mixture was allowed to stand for 24 h at room temperature. Thereafter, the precipitate formed was filtered off, suspended in 100 ml of ethanol, and saturated with HCl to complete dissolution. The solvent was evaporated to dryness in a vacuum, and the residue was washed with an ammonia solution in methanol and dissolved in 250 ml of heated water. The product was precipitated by adding 25 ml of a saturated $KClO_4$ solution. The resulting precipitate was filtered off and recrystallized from a methanol–ethanol mixture to give 125 mg of porphyrin **9**.

The metal complexes of brominated [6, 7] porphyrins were prepared by the procedure presented in [7].

Manganese complex **12** from Aldrich was used without additional treatment.

Table 2 summarizes the physicochemical characteristics of the synthesized compounds.

The following four clays were examined as inorganic supports for metal porphyrins: montmorillonite from Aldrich, Ca-montmorillonite from the Chernovtsy deposit (Ukraine), Na-montmorillonite from the Azkamar deposit (Uzbekistan), and kaolinite from the Prosyana deposit (Ukraine).

The catalytic oxidation of hydrocarbons was performed at room temperature in a flat-bottom flask equipped with a magnetic stirrer. A 10-ml portion of acetonitrile (Grade B, 99.9%, Venture Agency) containing $10^{-4}$ mol of a hydrocarbon, $10^{-4}$ mol of benzonitrile (as an internal standard), and $10^{-6}$ mol of a metal porphyrin catalyst (homogeneous oxidation) or 0.01 g of a powdered catalyst containing $10^{-6}$ mol of a metal porphyrin (heterogeneous oxidation) were placed in this flask.

**Table 2.** Characteristics of the synthesized porphyrins and their metal complexes

| Compound | Yield, % | Elemental analysis | | | $\lambda_{max}$, nm, ($\varepsilon \times 10^{-3}$) |
|---|---|---|---|---|---|
| | | found | empirical formula | calculated | |
| **4** | 24 | C 83.6, H 4.9, N 11.4 | $C_{43}N_5H_{29}$ | C 83.9, H 4.7, N 11.4 | 645(2.1), 589(3.3), 550(4.3), 515(10.8), 418(285) |
| **5** | 23 | C 80.9, H 4.4, N 13.5 | $C_{42}N_6H_{28}$ | C 81.3, H 4.5, N 13.6 | 644(2.7), 587(4.8), 548(6.1), 514(15.6), 417(388) |
| **8** | 98 | C 51.9, H 4.1, N 8.3 | $C_{56}H_{50}Cl_4N_8O_{16}Zn$ | C 51.8, H 3.9, N 8.6 | 607(6.2), 564(17.5), 438(189) |
| **9** | 76 | C 36.5, H 2.1, N 6.3 | $C_{56}H_{54}Br_8Cl_4N_8O_{16}$ | C 36.0, H 2.4, N 6.0 | 621(10.5), 465(133) |
| **10** | 84 | | $C_{47}H_{36}Cl_2MnN_5O_8$ | | 597(7.9), 566(11.6), 467(91) |
| **11** | 82 | | $C_{50}H_{44}Cl_3MnN_6O_{12}$ | | 597(7.0), 561(10.5), 462(77) |
| **1** | 74 | | $C_{56}H_{64}Cl_5FeN_8O_{20}$ | | 598(7.3), 423(89.3) |
| **2** | 89 | | $C_{56}H_{64}Cl_5MnN_8O_{20}$ | | 561(12.8), 462(121) |
| **6** | 90 | | $C_{56}H_{52}Br_8Cl_5FeN_8O_{20}$ | | 448(36) |
| **7** | 87 | | $C_{56}H_{52}Br_8Cl_5MnN_8O_{20}$ | | 678(7.8), 618(11.3), 482(62) |

An oxidizing agent was instantaneously added in an equimolar amount or in a three- to fivefold excess with respect to the substrate. We used $KHSO_5$ (Oxone) prepared from $(NH_4)_2S_2O_8$ according to the procedure presented in [9] as the oxidizing agent. The reaction was monitored by sampling until the complete deactivation of a catalyst.

The reaction products of hydrocarbon oxidation were analyzed by chromatography–mass spectrometry on a Kratos MS25RF instrument. The quantitative analysis of oxidation products was performed by GLC on a Tsvet 500M chromatograph (an SE-30 fused-silica capillary column, 25 m × 0.25 mm). The column temperature was programmed from 50 to 170°C at a heating rate of 10 K/min; the injector temperature was 250°C. Helium was used as a carrier gas; the inlet pressure of the carrier gas was 0.3 MPa.

X-ray diffraction analysis was performed on a DRON-1.5 X-ray diffractometer. The UV-spectroscopic studies of porphyrins and their metal complexes were performed on a Shimadzu UV-2100 spectrometer in an aqueous solution or in chloroform.

## RESULTS AND DISCUSSION

A study of the test clay samples demonstrated that only montmorillonite from Azkamar met the requirements for the specific surface area and the capacity for adsorbed metal porphyrins. The sorption capacity of the aluminosilicate was additionally increased by pretreatment with a titanium tetrachloride solution in hydrochloric acid according to the method proposed by Tichit *et al.* [10]. Coarse titanium hydroxide clusters entering the interlayer space of montmorillonite forced the layers apart and widened the mesopores.

The X-ray diffraction analysis of the Azkamar montmorillonite samples, which were promoted with $TiO_2$ and dried at 100°C, showed that titanium occurs as anatase in the interlayer space of the clay, and that the intercalated anatase disrupts the clay structure. As a result, the probability of a metal porphyrin penetrating into the interlamellar space increases because of the formation of microcracks and defects, and the interplanar spacings also increase. All the above factors increase the montmorillonite capacity for porphyrin.

Table 3 demonstrates that the interplanar spacing in montmorillonite promoted with titanium hydroxide clusters changed from 12.4 to 16.2 Å. The interplanar spacing in montmorillonite treated with titanium hydroxide changed from 16.2 to 18.2 Å after treatment with glycerol. This fact indicates that titanyl cations (tetravalent titanium in an aqueous medium) occupied positions in the interlamellar spaces of montmorillonite.

The montmorillonite–titanyl sample saturated with iron complex **1** at a rate of 0.1 mmol/g exhibited two series of basal reflections in the diffraction pattern: a weakly intense reflection with $d_{001}$ = 12.4 Å and a strongly intense reflection with $d_{001}$ = 15.0 Å. After saturating this sample with glycerol, a reflection with $d_{001}$ = 17.8 Å appeared, which corresponds to the montmorillonite–glycerol complex, and the intense reflection with $d_{001}$ = 15.0 Å remained unchanged.

The behavior of montmorillonite saturated with iron complex **1** indicated that a system was formed in which a part of montmorillonite layers did not sorb the porphyrin complex; this part contained only a water layer,

**Table 3.** Interplanar spacings in the Azkamar montmorillonite depending on the treatment procedure

| Sample | Interplanar spacings in the initial sample, Å | | Interplanar spacings in the sample saturated with glycerol, Å | |
|---|---|---|---|---|
| | values corresponding to the metal porphyrin intercalator | values corresponding to the low-molecular-weight intercalator (water) | values corresponding to the metal porphyrin intercalator | values corresponding to the low-molecular-weight intercalator (glycerol) |
| Azkamar montmorillonite in the initial state | – | 12.4 | – | 17.8 |
| Montmorillonite treated with titanium hydroxide | – | 16.2 | – | 18.2 |
| **1**/Montmorillonite + $TiO_2$ | 15.0 | 12.4 | 15.0 | 17.8 |
| **2**/Montmorillonite + $TiO_2$ | 14.3 | – | 14.4 | – |
| **6**/Montmorillonite + $TiO_2$ | 15.4 | – | – | 18.9 |
| **7**/Montmorillonite + $TiO_2$ | 16.4 | – | – | 20.0 |
| **10**/Montmorillonite + $TiO_2$ | 16.4 | – | – | 18.9 |
| **11**/Montmorillonite + $TiO_2$ | 16.5 | – | – | 18.8 |

which was then replaced by glycerol. At the same time, the interplanar spacing in the montmorillonite–iron porphyrin **1** complex remained unchanged after treatment with glycerol. This fact indicates that iron porphyrin **1** is tightly bound to montmorillonite.

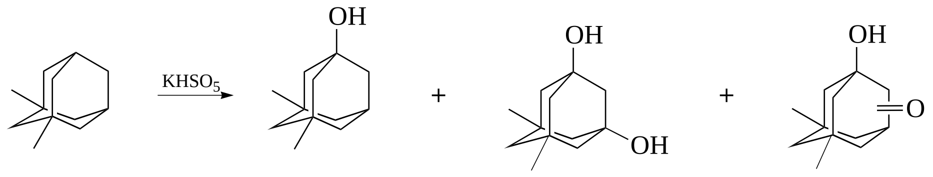
Peaks ascribed to regions that did not sorb a porphyrin complex were not observed in the X-ray spectra of other catalysts.

The X-ray diffraction study of manganese complex **2** demonstrated that the interplanar spacing equal to 14.3 Å remained unchanged after saturating the sample with glycerol, unlike other catalysts. This suggests that this porphyrin in the interlamellar spaces of montmorillonite bound mineral layers tightly and did not allow glycerol molecules to penetrate into the interlayer cavities.

The next stage was a study of the effect of the molecular structure of tetrapyridylporphyrins on the catalytic activity of their metal complexes in homogeneous and heterogeneous oxidation processes. The following parameters were varied: *meso*-substituents, which were partially replaced by phenyl groups, and β-substituents in the pyrrole rings of a porphyrin macrocycle, where hydrogen atoms were replaced by bromine atoms to a maximum degree.

Table 4 summarizes data on the activity of the synthesized metal porphyrin catalysts in the reaction of 1,3-dimethyladamantane oxidation.

A comparison between the catalytic activities (Table 4) of iron and manganese porphyrin complexes under conditions of homogeneous catalysis demonstrated that manganese porphyrin complexes are much more stable and active in the oxidation of cage and cyclic hydrocarbons by potassium peroxymonosulfate than analogous iron complexes.



Dimethyladamantane    1-Hydroxy-3,5-dimethyladamantane    1,3-Dihydroxy-5,7-dimethyladamantane    1-Hydroxy-5,7-dimethyladamantanone

Among synthesized manganese complexes **2**, **10**, and **11**, complex **2** was found most active in the reaction of 1,3-dimethyladamantane oxidation (Fig. 1). We believe that an increase in the number of electron-acceptor *N*-butylpyridyl *meso*-substituents in a metal porphyrin molecule enhances catalytic activity in hydrocarbon oxidation reactions.

On the addition of a threefold excess (in terms of the substrate) of the oxidizing agent, the conversion of 1,3-dimethyladamantane oxidized in the presence of

**Table 4.** Activity of the test catalysts in the reaction of 1,3-dimethyladamantane oxidation in acetonitrile ($T = 20 \pm 2$°C)

| Catalyst | Ratio of reactants (catalyst : substrate : oxidant) | Substrate conversion, % | Initial reaction rate, μmol $min^{-1}$ $cm^{-3}$ | Turnover number, mol/mol |
|---|---|---|---|---|
| **1** | 1 : 100 : 100 | 1 | 0.23 | 1 |
| **1**/Montmorillonite | 1 : 100 : 100 | 28 | 1.5 | 28 |
| **6** | 1 : 100 : 100 | 13 | 2.8 | 13 |
| **6**/Montmorillonite | 1 : 100 : 100 | 13 | 0.12 | 13 |
| **2** | 1 : 100 : 100 | 25 | 13 | 25 |
|  | 1 : 100 : 100* | 64 | 27 | 64 |
|  | 1 : 100 : 300 | 90 | 33 | 131** |
|  | 1 : 100 : 300* | 88 | 35 | 116** |
| **2**/Montmorillonite | 1 : 100 : 100* | 30 | 0.5 | 30 |
|  | 1 : 100 : 300 | 100 | 3.5 | 149** |
|  | 1 : 100 : 300* | 100 | 0.4 | 135** |
| **7** | 1 : 100 : 100 | 32 | 0.7 | 32 |
|  | 1 : 100 : 300 | 66 | 8.3 | 66 |
| **7**/Montmorillonite | 1 : 100 : 300 | 29 | 0.08 | 33** |
| **10** | 1 : 100 : 100 | 22 | 0.42 | 22 |
|  | 1 : 100 : 300 | 23 | 0.8 | 27** |
|  | 1 : 100 : 300* | 34 | 1.3 | 38** |
| **10**/Montmorillonite | 1 : 100 : 300 | 51 | 0.7 | 60** |
| **11**/Montmorillonite | 1 : 100 : 300 | 54 | 1.2 | 62** |

* In the presence of pyridine in an equimolar amount.

** Deep oxidation products of the substrate were additionally formed.

manganese complex **2** was 80% after 15 min, and it reached 90% after 1 h, when the catalyst was completely deactivated. Four products were detected in the reaction mixture; three of these products were identified as 1-hydroxy-3,5-dimethyladamantane, 1,3-dihydroxy-5,7-dimethyladamantane, and 1-hydroxy-7-dimethyladamantanone.

Note that the selectivity of 1,3-dimethyladamantane hydroxylation in the presence of this catalyst depends on the concentration of the oxidant (Table 4). With an equimolar amount (with respect to the substrate) of the oxidant, only 1-hydroxy-3,5-dimethyladamantane in 25% yield was detected in the reaction mixture.

The immobilization of manganese complex **2** on montmorillonite considerably increased catalyst stability. In the reaction of heterogeneous 1,3-dimethyladamantane oxidation with an excess of the oxidant, this catalyst underwent no degradation and deactivation even when 100% conversion of the substrate was attained; it catalyzed further oxidation of the reaction products to higher degrees. However, its activity turned out to be somewhat lower than that of a supported catalyst. Thus, for example, 90% conversion of the substrate was reached only 3.5 h after the onset of the reaction. The reaction products were the same as those of oxidation in the presence of the metal porphyrin dissolved in the reaction medium.

We found that, in the oxidation of 1,3-dimethyladamantane in the presence of the tetra-(4-*N*-butylpyridinium)porphyrin iron complex dissolved in the reaction mixture, the catalyst deactivated 7 min after the onset of the reaction, and the product yield was lower than 1%.

The substrate conversion was increased up to 28% by supporting iron complex **1** on montmorillonite. The bromination of the pyrrole rings in the porphyrin nucleus of the iron complex at β-positions increased the conversion up to 13%, as compared with the unbrominated catalyst under conditions of homogeneous oxidation.

Although catalyst stability was increased by the supporting of the brominated tetrapyridylporphyrin iron complex **6** on montmorillonite (the catalyst was not deactivated in 24 h), catalyst activity decreased as compared with the supported unbrominated catalyst, and the substrate conversion was as low as 13%. Thus, the supported unbrominated iron porphyrin catalyst was found most efficient in the reaction of 1,3-dimethyladamantane oxidation.

The introduction of bromine atoms into the β-positions of the pyrrole rings of manganese complex **2**

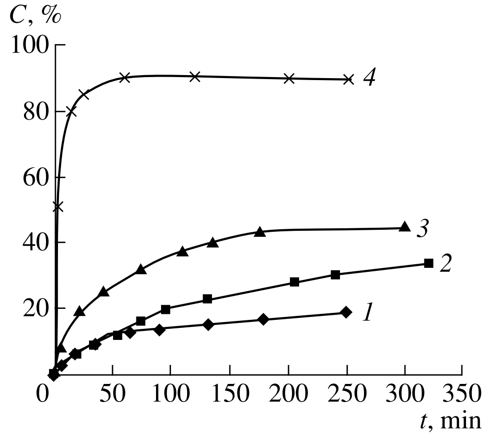
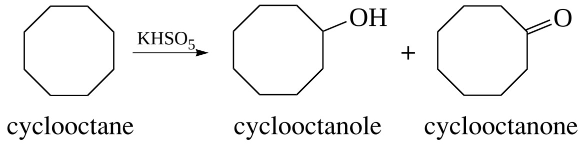


**Fig. 1.** Conversion (*C*) of 1,3-dimethyladamantane in the oxidation reaction with potassium peroxymonosulfate (*T* = 20°C; oxidant-to-substrate ratio of 3 : 1) as a function of time (*t*) on tetraarylporphyrin manganese catalysts with different *meso*-substituents: (*1*) **12**, (*2*) **10**, (*3*) **11**, and (*4*) **2**.

decreased the activity of catalyst **7** under conditions of homogeneous catalysis and, contrary to expectations, did not enhance the stability. Thus, in the oxidation of dimethyladamantane with a threefold excess of the oxidant with respect to the substrate, the substrate conversion was 66% after 1 h, and the catalyst was completely deactivated by that time.

In the supported manganese complexes of porphyrins, bromination decreased the activity and did not increase the stability of the test catalysts in comparison with unsupported complexes.

In addition to dimethyladamantane oxidation, we also studied the oxidation of cyclooctane by Oxone in acetonitrile in the presence of manganese complex **2**.



The substrate conversion attained in 3 h was 30%, and two products, cyclooctanol and cyclooctanone, were formed in 10 and 20% yields, respectively.

According to Maravin *et al.* [11], the manganese complexes of tetraarylporphyrins more efficiently catalyze hydrocarbon oxidation in the presence of nitrogen bases. The latter, which interact as axial ligands with the manganese atom, affect the polarization of the metal–oxygen bond and hence increase the probability of the transfer of a hydroxyl group to a carbon atom of the substrate.

In this study, we examined the effect of a nitrogen base (pyridine) on the activity of metal porphyrin catalysts. Pyridine was added to the reaction mixture in an equimolar amount with respect to the catalyst. We found that the presence of pyridine increased the activity of all of the dissolved manganese porphyrin catalysts and deactivated catalysts immobilized in montmorillonite. Thus, when pyridine was added to the reaction mixture in the homogeneous oxidation, the yield of the only reaction product 1-hydroxy-3,5-dimethyladamantane increased from 25 to 64%.

It is believed that the presence of pyridine, which actively coordinates manganese atoms in metal porphy-

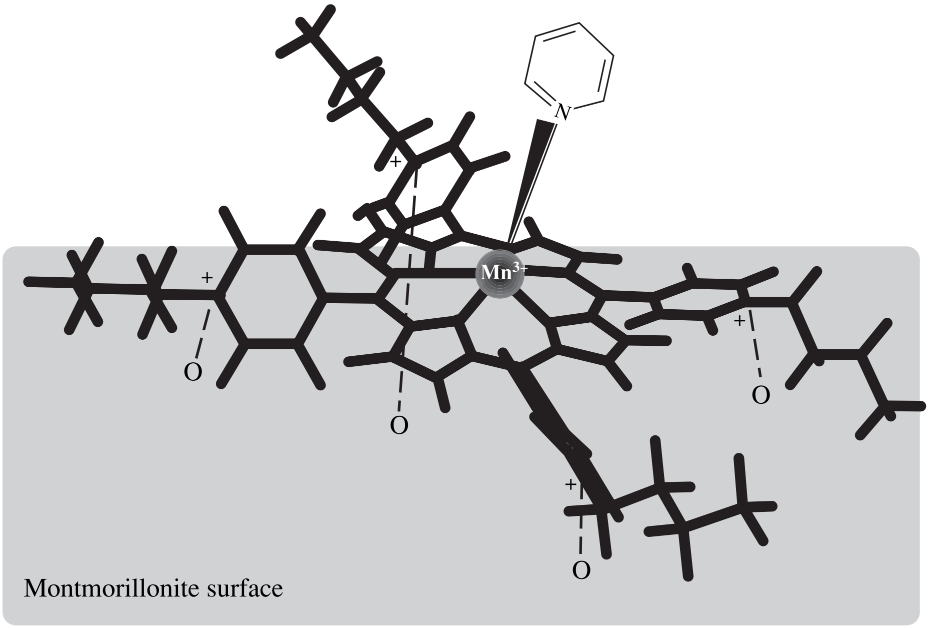


**Fig. 2.** Assumed structure of manganese complex **2** adsorbed on the surface of montmorillonite and coordinately bound to pyridine.

rin molecules that are bound to an aluminosilicate by two or more ionic bonds and whose molecular planes are oriented to the inorganic support, makes the active centers of the catalyst inaccessible to a substrate. However, an axial ligand in solution leaves a place sufficient for the interaction with the other side of a porphyrin molecule (Fig. 2).

## CONCLUSION

The immobilization of metal porphyrins on an aluminosilicate support decreases the initial reaction rate of substrate oxidation with the use of a manganese-containing catalyst. However, the oxidation of cycloparaffins can be performed more efficiently because of an increase in the stability of this catalyst. The introduction of bromine atoms into the β-positions of the pyrrole rings of manganese tetrapyridylporphyrins increases catalyst stability under conditions of homogeneous catalysis as compared with analogous unbrominated catalysts. However, this increase was not so significant as that observed in the series of tetraphenylporphyrin analogs [4]. The bromination of the manganese complex immobilized on montmorillonite slowed down the reaction of the transfer of active oxygen to the substrate to such an extent that the unbrominated metal porphyrin was found to be a more efficient oxidation catalyst.

The bromination of the tetra-(4-*N*-butylpyridinium)porphyrin iron complex increased catalyst activity and stability in homogeneous oxidation.

We found that the activity of metal porphyrin catalysts increases symbatically with the increasing number of butylpyridinium *meso*-substituents in the molecule of a porphyrin ligand.

The presence of pyridine in the reaction medium increases the activity of tetraarylporphyrin manganese complexes under homogeneous conditions and decreases the activity of the manganese complexes of the same porphyrins immobilized on montmorillonite.

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