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Catalysis of the Oxidative Chlorination of Aromatic Compounds with Substituted Iron Phthalocyanines

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Abstract—Iron phthalocyanine-catalyzed oxidative chlorination of aromatic hydrocarbons using the H_2O_2–HCl system led to the formation of the corresponding chlorine derivatives.

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The commonly used methods of chlorination of the aromatic hydrocarbons employ chlorination agents like chlorine, hypochlorites, and sulfuryl chloride. They are ecologically harmful and technologically inconvenient. The chloroperoxydase-catalysed H_2O + HCl system used by living organisms [1, 2] seems much more successful. But its non-catalyzed version requires a prolonged (15 h) keeping of the reactants in the 2,2,2-trifluoroethanol solution at room temperature [3] or refluxing for 6 h in methanol [4].

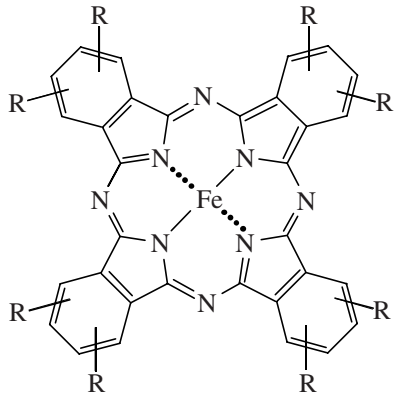
On the other hand it is known that iron phthalocyanines being structural analogs of prosthetic groups of the gem-containing oxidases actively catalyze the oxidation reactions (hydrosilylation, epoxidation, oxidative dimerization) of alkanes, alkenes, aromatic hydrocarbons, amines, and phenols [5–8] with oxygen, peroxides and peracids.

An attempt to use the substituted iron phthalocyanines as the chloroperoxidase models showed that the compounds containing positively charged substituents in the phenyl fragments of the macroring are extremely active catalysts of oxidative chlorination of aromatic compounds leading to the formation of the corresponding chlorine derivatives **I**.

$$A\text{–}H + Cl^- + H_2O_2 + H^+ \xrightarrow{PcFe} A\text{–}Cl + 2\,H_2O. \qquad (1)$$

Here A–H is the acceptor of halogen.

The catalysts were synthesized analogously to the corresponding aluminum and zinc complexes [9]. The



chlorination was carried out at room temperature by addition of H_2O_2 (the three-fold excess to the AH substrate) to the solution containing AH, the catalyst (0.17–1 mol%), and HCl. After 15 min the conversion of the substrate reached 30–100%. For example, the conversion of 2-methylnaphthalene in presence of 0.65 mol % of iron phthalocyanines **I–IV** reached 99%

for the catalyst **I**, 78% for **II**, 97% for **III**, and 24% for **IV**. The iron phthalocyanine-catalyzed chlorination proceeded selectively to give one or in some cases two isomeric monochlorinated derivatives. The only products of chlorination of 3,4-dimethoxytoluene, naphthalene, 2-methylnaphthalene and 2-methoxynaphthalene were 1-methyl-4,5-dimethoxy-2-chlorobenzene, 1-chloronaphthalene, 2-methyl-1-chloronaphthalene, and 2-methoxy-1-chloronaphthalene respectively. Phenol and anisidine gave a mixture of *ortho*- and *para*-chloroderivatives in the 1:1.2 and 1:3 ratio respectively. Chlorination of 2,3- and 2,6-dimethylnaphthalenes leads initially to the formation of 1-chloroderivatives. The addition of new portions of iron phthalocyanine and H_2O_2 caused further chlorination to 1,4-dichloro- and 1,6-dichloronaph-thalenes respectively. At performing the reaction under analogous conditions conversion (η, %) increased with the increase in the electron-donating character of substituent in the AH molecule and the increase in the amount of such substituents. For example, the conversion of naphthalene was 32%, of 2-methylnaphthalene 71%, and of 2-methoxynaphthalene 100%. 2,3-Dimethyl and 2,6-dimethylnaphthalenes attained 80% and 100% conversion respectively. These facts show that chlorinating agent has the electrophilic character (Cl^+). Interestingly, analogous species formed in H_2O_2–Cl^- system in the presence of chloroperoxidases [10].

EXPERIMENTAL

Commercial reagents and solvents were used in this study. Reaction mixture was analyzed by HPLC on a Hewlett-Packard 1100 device equipped with a UV detector (λ 254 nm), a Zorbax Eclipse 4.6×150 mm column with the dimethyl-*n*-octylsilane stationary phase, elution with the 6:4 acetonitrile–water mixture, flow rate 1 ml min^{-1}. Naphthalene was used as internal reference. Mass spectra were obtained on a Finnigan MAT INCOS-50 instrument. ^1H NMR spectra were taken on a Bruker AM300 (300 MHz) spectrometer. The analysis for C,H,and O in the reaction products was done on a Carlo Erba 1106 analyzer. Chlorine content was evaluated according to [11].

Oxidative chlorination of 2-methylnaphthalene *(general procedure).* To a solution of 2-methylnaphthalene (0.037×10^{-3} mol) in 1.9 ml of ethanol 0.5 ml of HCl (1.125×10^{-3} mol) and 0.05 ml of water solution of iron phthalocyanine **I** (0.11×10^{-6} mol) were added. The mixture obtained was treated while stirring with 0.05 ml of aqueous H_2O_2 (1.125×10^{-4} mol). The reaction product was identical to 2-methyl-1-chloronaphthalene prepared according to the procedure [12]. Yield 94% (HPLC). The product was subjected to column chromatography on silica gel, elution with chloroform–hexane mixture. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.6 s (3H, CH_3), 7.36 d (1H, H^3), 7.46–7.63 m (2H, H^6, H^7), 7.7 d (1H, H^5), 7.83 d (1H, H^4), 8.31 d (1H, H^8). Mass spectrum. *m*/*z* (I_{rel}, %): 176 (100) $[M]^+$, 141 (84). Found, %: C 74.57, H 5.22, Cl 20.07. $C_{11}H_9Cl$. Calculated, %: C 74.80, H 5.14, Cl 20.07.

2-Methoxy-1-chloronaphthalene was prepared from 2-methoxynaphthalene. Yield 99%. ^1H NMR spectrum, ($CDCl_3$), δ, ppm: 4.06 s (3H, OCH_3), 7.31 d (1H, H^3), 7.42 t (1H, H^6), 7.59 t (1H, H^7), 7.75–7.82 m (2H, H^4, H^5), 8.25 d (1H, H^8). Mass spectrum, *m*/*z* (I_{rel}, %): 192 (28) $[M]^+$, 177 (7), 149 (100), 126 (12), 114 (31). Found, %: C 68.28, H 4.44, Cl 18.10. $C_{11}H_9ClO$. Calculated, %: C 68.58, H 4.71, Cl 18.40.

2,3-Dimethyl-1,4-dichloronaphthalene was prepared from 2,3-dimethylnaphthalene, yield 95%, mp 152–153°C (EtOH). ^1H NMR spectrum, ($CDCl_3$), δ, ppm: 2.6 s (6H, CH_3), 7.56, 7.58 d.d (2H, H^6, H^7), 8.29, 8.31 d.d (2H, H^5, H^8). Mass spectrum, *m*/*z* (I_{rel}, %): 224 (100) $[M^- 1]^+$, 189 (98), 152 (55), 139 (4). Found, %: C 64.26, H 4.25, Cl 31.28. $C_{12}H_{10}C_{l2}$. Calculated, %: C 64.03, H 4.48, Cl 31.50.

2,6-Dimethyl-1,5-dichloronaphthalene was prepared from 2,6-dimethylnaphthalene, yield 95%, mp 133–134°C. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.59 s (6H, CH_3), 7.4 d (2H, H^3, H^7). 8.12 d (2H, H^4, H^8). Mass spectrum, *m*/*z* (I_{rel}, %): 224 (100) $[M - 1]^+$, 189 (66), 152 (27), 139 (4). Found, %: C 64.25, H 4.29, Cl 31.29. $C_{12}H_{10}Cl_2$. Calculated, %: C 64.03, H 4.48, Cl 31.50.

1-Methyl-4,5-dimethoxy-2-chlorobenzene was prepared from 3,4-dimethoxytoluene, yield 99%, mp 33–34°C (EtOH). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.3 s (CH_3), 3.85 s (6H, OCH_3), 6.7 s (H^2), 6.83 s (H^5). Mass spectrum, *m*/*z* (I_{rel}, %): 186 (100) $[M]^+$, 171 (44), 143 (40), 125 (18), 108 (78), 93 (34), 77 (72). Found, %: C 58.19, H 5.91, Cl 18.76. $C_{11}H_9Cl$. Calculated, %: C 57.92, H 5.94, Cl 19.0.

o- and *p*-Chloro derivatives of phenol and anisol as well as 1-chloronaphthalene according to HPLC data were identical to the commercial samples.

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REFERENCES

1. Liu, T.-N.E., Timkulu ,T.M., Geigert, J., Wolf, R., Neidleman, S.L., Silva, D., and Hunter-Cevera, J.C., *Biochem. Biophys. Res. Commun*., 1987, vol. 142, no. 2, p. 329.
2. Burd', V.N., Van, Pe K.-Kh., Lingens, F., and Voskoboev, A.I., *Bioorg. Khim*., 1992, no. 18, p. 1002.
3. Ben-Daniel, R., Visser, S.R., Shaik, S., and Neumann, R., *J. Am. Chem. Soc*., 2003, vol. 125, no. 40, p. 12116.
4. Barhate, N.V., Gajare, A.S., Wakharkar, R.A., and Bedekar, A.V., *Tetrahedron Lett*., 1998, vol. 39, no. 35, p. 6349.
5. Kaliya, O., Lukyanets, E., and Vorozhtsov G.J., *Porphyrins and Phthalocyanines*, 1999, vol. 3, no. 7, p. 592.
6. Russian Patent no. 2045531, 1995; *Byull. Izobret*., 1995, no. 28.
7. Russian Patent no. 2260583, 2005; *Byull. Izobret*., 2005, no. 26.
8. Hadasch, A., Sorokin, A., Rabion, A., and Meunier, B., *New J. Chem.*, 1998, no. 1, p. 45.
9. Russian Patent no. 2282646, 2005; *Byull. Izobret*,. 2006, no. 24.
10. Shevelkova, A.N., Sal'nikov, Y.I., Kuz'mina, N.L., and Ryabov, A.D., *FEBS Lett*., 1996, vol. 383, no. 3, p. 259.
11. Gel'man, N.E., Terent'eva, E.A., Shanina, T.M., Kiparenko, L.M., and Rezl, V., *Metody kolichestvennogo organicheskogo elementnogo mikroanaliza* (Methods of Quantitative Organic Elemental Analysis), Moscow: Khimiya, 1987, p. 229.
12. Fozard, A. and Bradsker, C.K., *J. Org. Chem*., 1966, vol. 31, no. 11, p 3683.