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Homogeneous Oxidation of Aromatics in Nucleus with Peracetic Acid Catalyzed by Iron and Manganese Phthalocyanine Complexes

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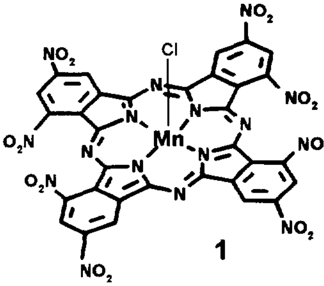
Abstract: the reaction of naphthalene and methylnaphthalenes with peracetic acid catalyzed by Mn(III) (**1**) or Fe(II) (**2**) octanitrophthalocyanines in CH_3CN at 20°C produces 1,4-naphthoquinones with 35-62% yields. The corresponding 2,3-epoxide-1,4-endoperoxides are proposed as intermediate in reaction catalyzed by **1**.

As cytochrome P-450, some metal complexes of porphyrins (PorM) were found to act as good catalysts of oxygen atom transfer from various single-oxygen atom donors such as hydroperoxides, peracids etc. with formation of epoxides from alkenes and alcohols from alkanes[1]. Earlier[2,3] we have shown the efficiency of porphyrin aza analogues (APM) - tetraazaporphines and substituted phthalocyanines (RPcM, M=Fe, Co) in cyclohexane oxidation by cumene hydroperoxide. Recently[4], catalytic activity both of PorMnCl and APMnCl was demonstrated in olefin stereoselective epoxidation by peracetic acid.

To our knowledge, there are a few of data about aromatics oxidation in nucleus catalyzed by PorM. The possibility of naphthalene hydroxylation to naphthols by H_2O_2 was demonstrated for PorFe[5], but experimental conditions (large excess of substrate) provide less than 1% of naphthalene conversion. Methoxynaphthalenes may be converted to corresponding 1,4-quinones (yields up to 55%) by Mg-perphthalate in the presence of PorFe[6]. There are some reports about modelling of the cytochrome P-450 enzymes function with non-porphine transition metal complexes[7-11]. So, some anthracenes were oxidized to corresponding 9,10-anthraquinones by mixture of AcOOH and H_2O_2 with up to 95% yield[8], and perfluorobenzene was converted by CF_3CO_3H to oxalic acid derivatives[7] in the presence of V(+5) complexes. Some polyether complexes of Fe(+2) catalyze benzene hydroxylation to phenol by H_2O_2[10]. Naphthalene was converted to 1,4-naphthoquinone with 40% yield by oxygen with Pd(+2) and Cu(+2) salts supported on silica[9]. Complex $ReO_3(CH_3)$ catalyzes 2-methylnaphthalene oxidation with peracetic acid to 2-methyl-1,4-naphthoquinone (4 h, 40°C) with 50% yield[11]. Nevertheless, all these data do not allow to consider the problem of aromatics oxidation in nucleus as solved even partly from the point of view both of mechanism and technological applications.

In this paper[12] we report the efficient catalytic oxidation of naphthalene (Nf), 2-methylnaphthalene

(MeNf) and 2,3-dimethylnaphthalene (Me_2Nf) in mild conditions (acetonitrile, 20°C) with peracetic acid (AcOOH) in the presence of Mn or Fe 3,5-octanitrophthalocyanines ($NO_2PcMnCl$ (**1**), NO_2PcFe) giving corresponding 1,4- quinones with yields 35-62 %. Non-catalyzed naphthalene oxidation by peracetic acid (17 days, 20°C) yields o-carboxycinnamic acid as a final product[13]. Nitrosubstituted PcM were chosen due to the fact[3,14] that PcM stability towards oxidants increases with growing substituent electronegativity. These complexes were synthesized following known methods[15,16]. In the case of NO_2PcFe, two types of complexes were tested: acidic $H^+(NO_2PcFe)X^-$ and μ-oxodimeric $(BH^+)_2(NO_2PcFeOFePcNO_2)^{2-}$ (**2**, B = acetone, CH_3CN, Et_3N)[17], the last one being twice more active in naphthalene oxidation to 1,4-naphthoquinone. In further study complex **2** was used as catalyst. Peracetic acid solutions (1,5-1,9 M) in acetic acid were prepared from 30% H_2O_2 and acetic anhydride using earlier developed simple method[7]. These solutions do not contain H_2O_2 or diacetyl peroxide, thus preventing the interference of radical-producing side reactions in the presence of catalysts[18,19].



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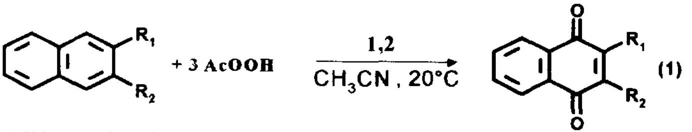
Oxidation of 1×10^{-3}-0,2 M Nf, MeNf and Me_2Nf solutions was carried out by 3-4 fold molar excess of peracetic acid in the presence of **1** or **2** with 100% substrate conversion. The products of naphthalenes oxidation are the corresponding 1,4-naphthoquinones (reaction 1) and, supposedly, polymers of oxygenated naphthalene derivatives isolated as brown-red precipitates. Naphthoquinones structures were established by comparison of isolated reaction products (extraction with hexane followed by chromatography) with authentic samples (HPLC, GC); in the case of MeNF and Me_2Nf any isomers of quinones were detected both in reaction solutions and in isolated products. As shown in **Table 1**, yields of 1,4-quinones depend on substrate:catalyst ratio even at full substrate conversion, exhibiting the complex character of the reaction under study. In the case of **2** oxidation was carried out in $CH_3CN/AcOH$ (85/15) mixture because of side radical AcOOH decomposition at acetic acid content less than 8 %.



a) Nf, $R_1 = R_2 = H$; b) MeNf, $R_1 = CH_3$, $R_2 = H$; c) Me_2Nf, $R_1 = R_2 = CH_3$

Aromatics oxidation with **1** has some peculiarities. Quinones yield values determined at the end of reactions (initial yield) are 1,5-5 times lower than after heating of neutralized reaction mixtures (Table 1), suggesting thermally unstable intermediates formation in naphthalenes oxidation. In the case of naphthalene oxidation catalyzed by **1** treatments of reaction mixture by $NaHSO_3$, then 30 % aqueous H_2O_2 yields 2,3-dihydroxy-1,4-naphthoquinone (iso-naphthazarin, reaction 2). The latter one is known to be formed by

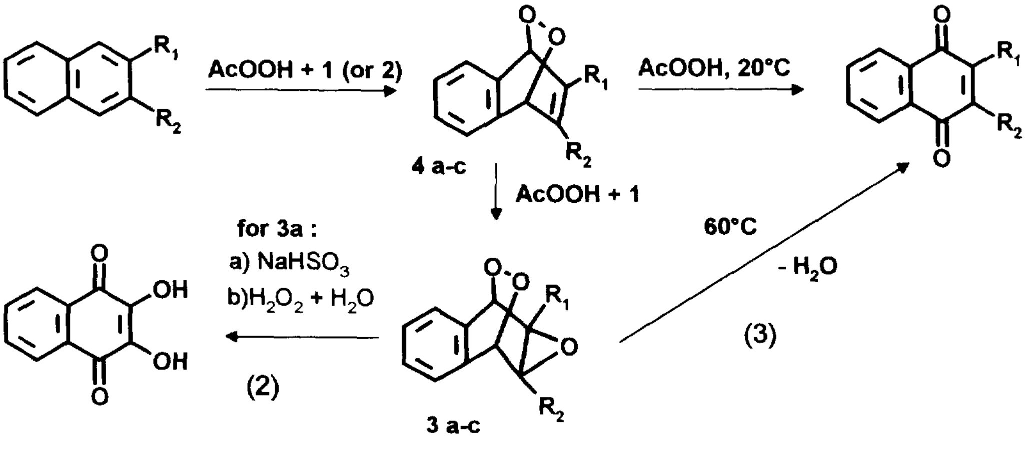
Table 1 - Yields of 1,4-quinones (η_Q) in Nf, MeNf and Me_2Nf oxidation with AcOOH in the presence of 1 and 2 (reaction times 15-90 min, GC and HPLC data).

Substrate (sub)	Catalyst (cat)	$[sub]_0$: $[cat]_0$, M/M	η_Q,%	Substrate (sub)	Catalyst (cat)	$[sub]_0$: $[cat]_0$, M/M	η_Q,%
Nf	1 [a]	23:1 [b]	51,7 (10,6) [c]	Nf	2 [d]	133:1 [e]	35,0
MeNf	1 [a]	23:1 [b]	55,0 (19,8) [c]	MeNf	2 [d]	133:1 [b]	62,0
Me_2Nf	1 [a]	23:1 [b]	59,5 (36,2) [c]	Me_2Nf	2 [d]	133:1 [b]	47,0
Nf	1 [a]	16:1 [b]	52,0 (11,0) [c]	MeNf	2 [d]	166:1 [b]	52,0
Nf	1 [a]	40:1 [b]	42,0 (10,0) [c]	MeNf	2 [d]	222:1 [b]	41,0
Nf	1 [a]	80:1 [b]	30,0 (9,0) [c]	MeNf	2 [d]	333:1 [b]	25,0
Nf	1 [a]	160:1 [b]	22,0 (10,0) [c]	MeNf	2 [d]	667:1 [b]	12,0

a) $[AcOOH]_0$:$[substrate]_0$ = 4:1; b) 100% substrate conversion. η_Q values are calculated on reacted substrate; c) yields of 1,4-quinones were determined after heating (60°C, 30 min) of neutralized reaction mixtures. In parentheses initial quinone yield values are given; d) $[AcOOH]_0$:$[substrate]_0$=3,2:1; e) 88 % naphthalene conversion.

hydrolysis of 2,3-epoxy-2,3-dihydro-1,4-naphthoquinone in aerated aqueous solutions[13]. So, the intermediate formation of 2,3-epoxy-1,2,3,4-tetrahydronaphthalene-1,4-endoperoxide (**3a**) can be proposed with its transformation to 1,4-naphthoquinone via O-O bond cleavage and H_2O evolving (reaction 3). The possibility of two oxygen atoms insertion into the molecule of aromatic compound by oxygen containing forms of catalysts has been discussed for catalytic systems V(+5) and CF_3CO_3H or AcOOH[7,8].

We have supposed that both (**3a-c**) and initial 1,4-naphthoquinones were formed from the same intermediates (**4a-c**). In this case (**3a-c**) formation must be complicated for MeNf and Me_2Nf due to sterical



hindrances in comparison to Nf. Therefore, initial 1,4-naphthoquinones yields would increase in the row Nf - MeNf - Me_2Nf. The experimental data (Table 1) are in accordance with this idea, suggesting that C_2 and C_3 atoms are involved in formation of intermediate (**3a-c**). The fact that (**3a-c**) are not formed in the reactions catalyzed by **2** may be explained by less reactivity of oxygen containing forms of **2** (supposedly oxene complex) towards double bond in (**4a-c**) in comparison to Mn-containing catalyst.The mechanism of 1,4-naphthoquinone formation in Nf oxidation in the presence of **1** will be discussed more in detail in the next communication.

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