Naphthalene oxidation by peracetic acid catalysed by Mn^{3+} porphinoid complexes

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A comparison of the oxidation of naphthalene and its d^8-derivative by peracetic acid catalysed by Mn^{3+} tetranitrotetra-*tert*-butyltetraazaporphine allowed us to refine both the mechanisms of 1,4-naphthoquinone and 1-naphthol formation and the structures of the final products of 1-naphthol oxidation.

The oxidation of aromatic compounds in nuclei is a subject of continual interest; in the last decade, certain success has been achieved in the resolution of this problem. It was reported on 2-methylnaphthalene conversion to 2-methyl-1,4-naphthoquinone (menadione) in 45–65% yield by means of different oxidants [H_2O_2,[1] $(Me_3SiO)_2$,[2] $KHSO_5$,[3] AcOOH[4–6]] and catalysts of both non-porphinoid (Re^{7+} oxo complexes[1,2]) and porphinoid structure (Mn and Fe complexes of substituted porphyrin[3] and azaporphines[4–6]). Previously, we found the effectiveness of Mn^{3+} azaporphines in naphthalene (Nph) oxidation by peracetic acid to the corresponding *para*-quinones and oligomeric products in acetonitrile–acetic acid solutions. Of studied complexes {3,5-octanitrophthalocyanine (ONPcMnCl),[4,5] tetra-R-tetra-*tert*-butyltetraazaporphine [RTAPMnCl; R = NO_2 (**1**), Br][6]}, tetraazaporphine **1** was the most active in the formation of *para*-quinones. We hypothesised that under the reaction conditions naphthalene oxidation proceeds *via* two parallel paths with the participation of oxene and peroxide Mn complexes with the formation of 1-naphthol (as a primary product, NOH) and 1,4-naphthoquinone (Q), respectively. Here, we describe the results of the comparative oxidation of naphthalene and its deuterated analogue ($C_{10}D_8$) in **1** + AcOOH catalytic system.

Previously, we found that the kinetics of 1-naphthol formation was almost the same in the naphthalene oxidation in the catalytic systems AcOOH + Mn^{3+}-porphinoids (PMnX) [P = *meso*-tetra(2,6-dichloro-6-R-phenyl)porphyrins (RTDCPPMnCl, R = = MeO, H, Br, Cl, NO_2),[7] tetraazaporphines (RTAPMnCl, R = H, $PhSO_2$, **1**),[8] phthalocyanine (ONPcMnCl)[5]]. The epoxidation of *cis*-olefins in the same catalytic systems was found to be highly stereospecific,[7,8] which is commonly accepted as a proof of the formation of highly-reactive Mn^{5+}-oxene {[PMn^{5+}(O)(L)](X)}. Nevertheless, comparative and competitive oxidation of naphthalene and olefins[7,8] revealed that naphthalene hydroxylation is fulfilled by another catalytic intermediate, presumably by the Mn^{4+}-oxene of a porphinoid π-cation radical {[$^{+\cdot}$$PMn^{4+}$(O)(L)](X), **2**; L = AcOH}. The intimate mechanism of oxygen atom transfer from oxene **2** to the naphthalene molecule, though, was not established. As reported, hydrocarbon hydroxylation in both actual enzymes and model systems can occur *via* either H-atom abstraction[9] or the insertion of an oxygen atom of metallo-oxene into the C–H bond with the intermediate formation of a pentacoordinated carbon atom.[10] To discriminate some of the proposed possibilities, we compared the rates of 1-naphthol formation in the course of $C_{10}H_8$ and $C_{10}D_8$ oxidation by AcOOH + **1**. Actually, if an oxygenated product is formed with H-atom abstraction from a substrate molecule, its formation should be characterised by a significant kinetic isotope effect (KIE).

The initial rate of 1-naphthol formation (W^{in}_{NOH}) exhibits the Michaelis–Menten kinetics [Figure 1; equation (1)], indicating the participation of a hydroxylating moiety in both 1-naphthol formation and catalyst destruction [rate constants k_N and k_d, respectively; unimolecular catalyst degradation is considered for simplicity].

If 1-naphthol formation had been fulfilled with H-atom abstraction from a molecule of naphthalene, then at its low concentrations [equation (2)] the W^{in}_{NOH} value should have been much lower for $C_{10}D_8$ than for $C_{10}H_8$ ($k_N^{deut} << k_N^{nondeut}$). This contradicts the experiment: as shown in Figure 2, the kinetic curves of 1-naphthol formation are identical for both substrates.

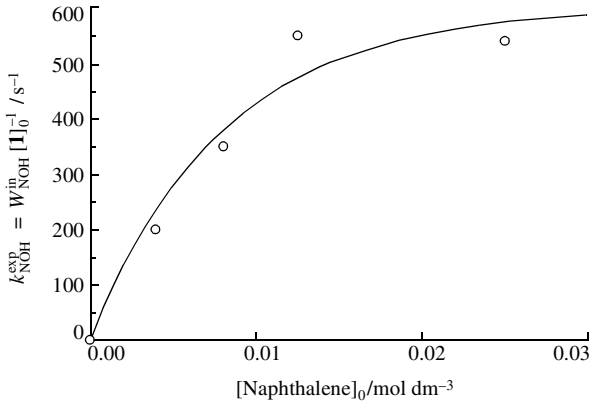


Figure 1 Partial rate (W^{in}_{NOH} / [**1**]) of 1-naphthol formation as a function of naphthalene concentration. [**1**] = (0.5–2)×10^{-8} mol dm^{-3}, [AcOOH] = = 0.05 mol dm^{-3}. MeCN + AcOH (0.5 M).

$$W_{NOH} \sim \frac{k_N[\text{Naphthalene}]_0}{k_d + k_N[\text{Naphthalene}]_0} \quad \text{at } k_d > k_N[\text{Naphthalene}]_0 \qquad (1)$$

$$W_{NOH} \sim \frac{k_N}{k_d}[\text{Naphthalene}]_0 \qquad (2)$$

These data allow us to reject the radical, oxygen-rebound and concerted non-synchronous mechanisms (the last is characterised by a high KIE value of the first intermediate transformation to the final product[10]). The proposed[11] intermediate formation of 1,2-arene oxides last time is considered rather questioned both for mimicking[3] and enzyme-depending systems[12] and does not occur under the reported conditions because of the absence of isomeric 2-naphthol in the RTAPMnCl-catalysed reactions.† This

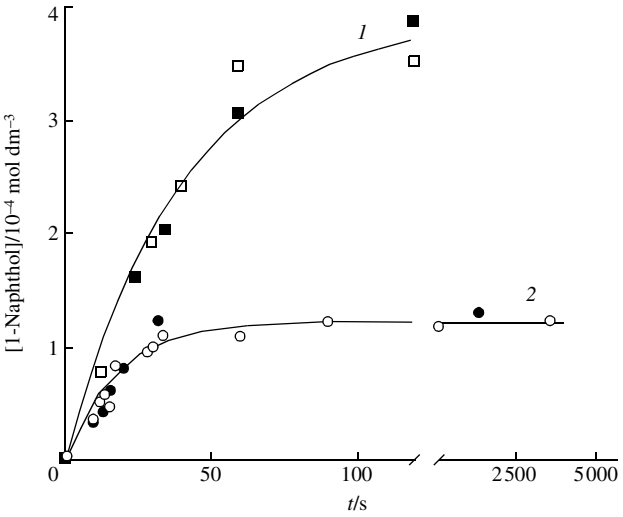
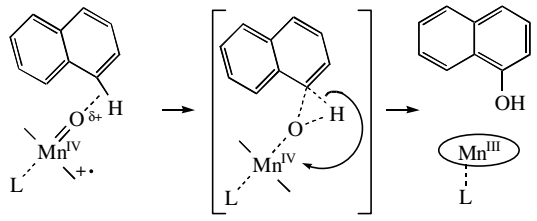
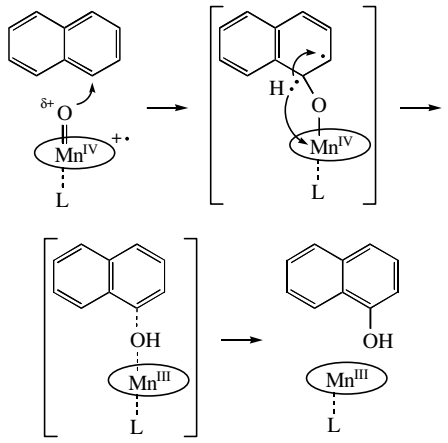


Figure 2 Kinetic curves of 1-naphthol formation in the reaction of $C_{10}H_8$ (open squares and circles) and $C_{10}D_8$ (solid squares and circles) oxidation by AcOOH catalysed by **1**. (*1*) [**1**] = 1×10^{-8} mol dm^{-3}, [$C_{10}H_8$] = [$C_{10}D_8$] = = 0.025 mol dm^{-3}, [AcOOH] = 0.05 mol dm^{-3}, [AcOH] = 0.5 mol dm^{-3}; (*2*) [**1**] = 2×10^{-8} mol dm^{-3}, [$C_{10}H_8$] = [$C_{10}D_8$] = 0.004 mol dm^{-3}, [AcOOH] = = 0.025 mol dm^{-3}, [AcOH] = 0.25 mol dm^{-3}.

last also contradicts with the mechanism of one-electron naphthalene oxidation followed by proton abstraction. We suggest that the discussed reaction occurs by a 'concerted' mechanism of oxygen insertion into the C_{arom}–H bond or *via* the intermediate formation of the σ-adduct PMn–O–C_{arom}, which has been proposed[3] for Mn(Fe) porphyrin-catalysed oxidation of 2-methylnaphthalene by $KHSO_5$ (Figure 3).



(*a*) Concerted mechanism

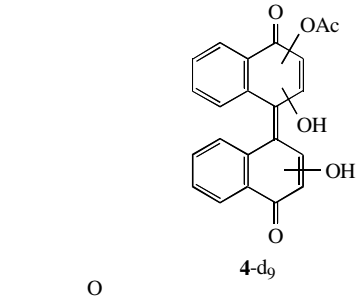


(*b*) Mechanism with σ-adduct formation

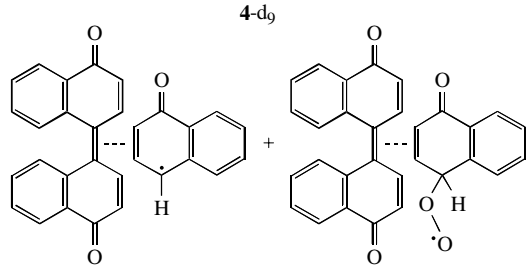
Figure 3 Possible mechanisms of naphthalene hydroxylation by peracetic acid in an acetonitrile–acetic acid solution catalysed by Mn^{III} porphinoid complexes [$PMn^{III}(L)$](X), P = substituted porphyrins, porphyrazines, phthalocyanines; L = AcOH; X = Cl^-, AcO^- (not shown).

Under the specified conditions, firstly formed 1-naphthol undergoes further oxidation to oligomers;[5] the nature of these products depends on the substrate concentration.

The oxidation of naphthalene or 1-naphthol at low concentrations (< 0.01 mol dm^{-3}) leads to a brownish residue, which was isolated as a main product in the reactions catalysed by RTDCPPMnCl and Mn^{3+} tetra-*tert*-butyltetraazaporphine and as a by-product in the reactions catalysed by ONPcMnCl and **1**. Capillary electrophoresis, IR spectroscopy and HPLC (4–5 non-resolved peaks with V_R higher that that of naphthalene; Separon C_{18} reverse phase, 10–100% aqueous acetonitrile) and ^{1}H NMR (8–9 peaks at 1.8–2.4 ppm; ~20 peaks at 7.5–8.0 ppm; Bruker 80 MHz or 300 MHz) indicate that this residue is a mixture of hydroxylated and acetylated derivatives of naphthoxy radical coupling products, whose composition depends on AcOOH concentration. At a fourfold excess of the oxidant ([AcOOH]:[Nph]:[ONPcMnCl] = 640:160:1, $[Nph]_0$ = 0.004 M), the isolated precipitate exhibited *m/z* 286, 374, 426, 442, 456, 472 and 486 (FAB MS data), which correspond to hydroxy, acetoxy and naphthoxy derivatives of 1,1′-dinaphthoquinone-4,4′ **3**. At [AcOOH]:[Nph] = 1.5, naphthoxy-**3** is not formed: mass ions (*m/z* 333, 347, 375, 389, 403, 418 and 432) correspond to acetylated and hydroxylated derivatives of both **3** and 1,1′-dihydro-**3**. The determination of the exact composition of such complex mixtures needs additional research; the reported data, though, fit well with the hypothesis on the radical mechanism of 1-naphthol oxidation with H-atom abstraction followed by the coupling of the formed naphthoxy radical, oxidation to **3**, its acetylation and hydroxylation. In terms of this hypothesis, the oxidation of $C_{10}D_8$ instead of $C_{10}H_8$ under the same conditions should yield a lower number of oligomers. Really, MALDI analysis‡ of the spent reaction solution of $C_{10}D_8$ oxidation revealed only dimer **4** and its 4,4′-dihydroxy derivative (*m/z* 191.9 and 192.9, *z* = 2; Figure 4).



4-d_9



5 **5a**

Figure 4 The proposed structures of the oligomeric products of naphthalene oxidation.

When 0.1 M naphthalene or 1-naphthol was oxidised by dropwise addition of AcOOH to a mixture of the catalyst and the substrate, the single product was a violet precipitate unstable both in solution and in the solid state. Based on the data of elemental analyses (13–16% oxygen content per naphthalene unit), MALDI§ spectra (*m/z* 426.3, 286), ^{1}H NMR (only broadened peaks at 7.0–8.0 ppm) and IR spectra (peaks corresponding to the C–OH and C=O bands), we suppose this compound to be a mixture of 1,1′-dinaphthoquinone-4,4′ complexes with the naphthyloxy radical and its oxygenated form (**5**, $C_{30}H_{19}O_3$, *M* = 427; **5a**; Figure 4).

Our conclusion on 1-naphthol radical oxidation agrees with the results on 2,3,5-trimethylphenol (TMP) oxidation under the same reaction conditions ([AcOOH]:[TMP]:[ONPcMnCl] = 6400:4000:1). In this case, phenoxy radical coupling is sterically hindered, and exhaustive TMP oxidation leads to the formation of 2,3,5-trimethyl-1,4-benzoquinone in a yield higher than 95% (based on the oxidant used).

As we found previously,[4–6] in the oxidation of naphthalene and its methyl derivatives in APMnX + AcOOH catalytic systems, the quinone yield determined at the end of the reaction (η^{in}) increases significantly (η^{therm}) after heating (40–70 °C) or continuous storage of neutralised reaction solutions at 20 °C. HPLC analysis before heating revealed an unidentified peak of a polar compound, the intensity of which decreases on heating with a simultaneously increasing peak of *para*-quinone, thus indicating the formation of quinone precursor **6**.¶ Here, we report the study of 1,4-naphthoquinone-d_6 (Q_d) formation in the reaction $C_{10}D_8$ + AcOOH + **1**.

As in the case of $C_{10}H_8$, the formation of 1,4-naphthoquinone-d_6 (Q_d)†† is preceded by the formation of a **6**-type inter-

† The minor formation of 2-naphthol (10% to 1-naphthol) in RTDCPPMnCl[7] and ONPcMnCl[5] dependent reactions might be explained by a lower electrophilicity of the corresponding Mn-oxenes as compared with their tetraazaporphine analogues.

‡ 'Mass spectrum with matrix assisted laser desorption ionization' (MALDI); under the conditions of MALDI analyses (2,5-dihydroxybenzoic acid or sinapinic acid as a matrix), the authentic samples of 1,4-naphthoquinone and 2-methyl-1,4-naphthoquinone were determined as the 1,4-dihydroxy derivatives. We suppose also partial reduction of **4** at MALDI spectrum registration and attribute a peak *m/z* 192.9 (*z* = 2) to its 4,4′-dihydroxy derivative.

§ 2,4,6-Trihydroxyacetophenone was used as a matrix.

¶ Presumably, HPLC analysis detects not intermediate **6**, but a product of its transformation under analytical conditions.

†† Thermal transformation of $\mathbf{6}_d$ to 1,4-naphthoquinone-d_6 was proved by HPLC and MALDI.

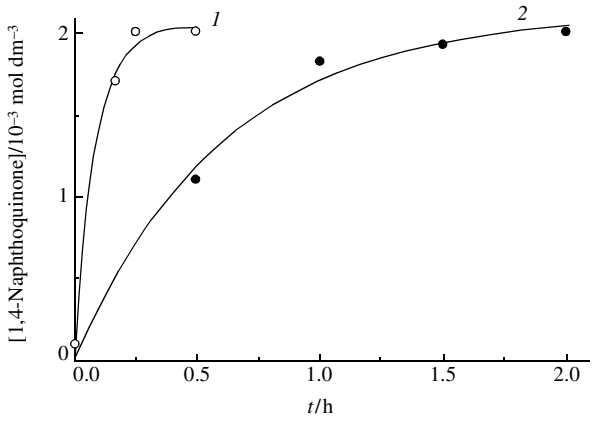


Figure 5 Time dependence of 1,4-naphthoquinone formation on heating (50 °C) the neutralised (with solid Na_2CO_3) reaction solution after exhaustive oxidation of $C_{10}H_8$ (open circles) and $C_{10}D_8$ (solid circles). $[C_{10}H_8] = [C_{10}D_8] = 0.004$ mol dm^{-3}, [**1**] = 5×10^{-6} mol dm^{-3}, [AcOOH] = 0.002 mol dm^{-3}, [AcOH] = 0.02 mol dm^{-3}.

mediate (**6**$_d$). The rates of $C_{10}D_8$ and $C_{10}H_8$ disappearance were found to be equal; taking into account the independence of the 'oxenoid' pathway on deutero substitution, this evidences the absence of a significant isotope effect at the stage of **6**$_d$ formation. It seems that all H atoms of the substrate are kept in the molecule of a quinone precursor. On the contrary, the transformation of **6**$_d$ to 1,4-naphthoquinone-d_6 is significantly hindered as compared with the non-deuterated analogue: the total time of heating the neutralised reaction mixture to provide a maximum quinone yield (50%) is eight times longer for $C_{10}D_8$ than that for $C_{10}H_8$ (Figure 5).

Moreover, in the case of $C_{10}D_8$ at the beginning of gentle heating (40–50 °C; HPLC, TLC),‡‡ 1,4-dihydroxynaphthalene, in addition to a quinone, was detected, thus elucidating two steps of **6**$_d$ transformation to the quinone. Presumably, 1,4-dihydroxynaphthalene-d_8 is the first product of **6**$_d$ decomposition, and its further oxidation to 1,4-naphthoquinone-d_6 is not accompanied by an isotope effect due to quick OD–OH exchange. We suppose that the high isotope effect of *para*-quinone formation from **6** reflects the breakage of the C_{arom}–H bond in the latter at the stage of 1,4-dihydroxynaphthalene formation.

Based on the data on the comparative and competitive oxidation of aromatic and aliphatic hydrocarbons,[4–6] we proposed the structure of 1,4-peroxo-2,3-epoxy-1,2,3,4-tetrahydronaphthalene for intermediate **6**. The data reported here agree with this attribution and with the mechanism of **6** formation (Scheme 1, stage 8).

Intermediate **6**$_d$ is rather stable only in MeCN solutions; we failed to isolate it in a solid state. Under conditions of MALDI spectrum measurements, **6**$_d$ was also decomposed: the spent unheated reaction solution shows a peak at *m*/*z* 158.9 with $z = 2$ corresponding to a complex of 1,4-dihydroxynaphthalene-d_6 with naphthol-d_7 [$(C_{10}D_6H_2O_2)\cdot(C_{10}D_7HO)$, MW 317.4].§§ In terms of our hypothesis on the structure of **6**, these compounds could be derived from two molecules of **6** by a laser pulse with the withdrawal of an oxygen atom or an O–O fragment, respectively.

In summary, we specified the stages of formation of 1,4-naphthoquinone, 1-naphthol and its oxidative products (Scheme 1, stages 7–10 and 3–5, respectively) in the proposed mechanism of aromatics oxidation by peracetic acid catalysed by Mn^{3+} azaporphines.

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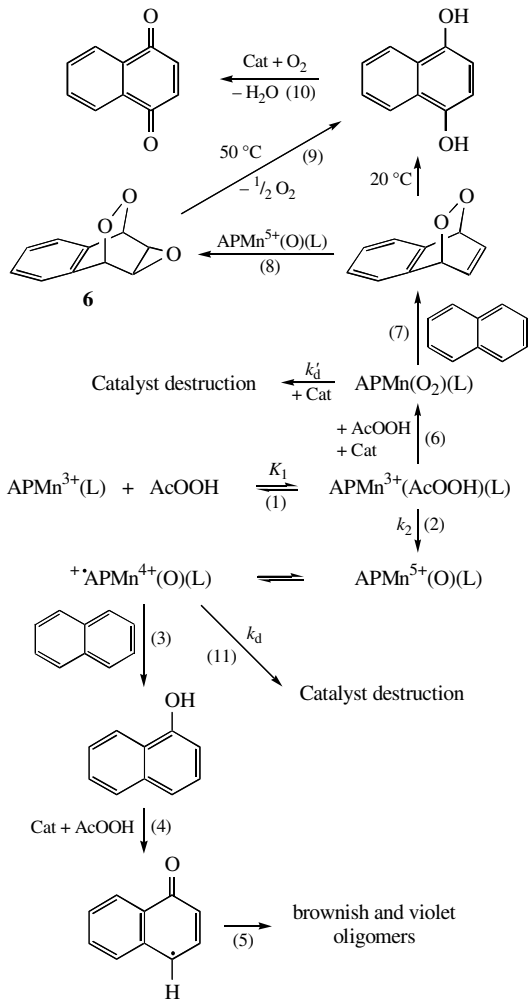
‡‡ The oxidation of 1,4-dihydroxynaphthalene to 1,4-naphthoquinone by oxygen in the presence of Mn complexes was demonstrated in independent experiments. In the case of $C_{10}D_8$, the heating of the neutralised reaction mixture at 75 °C leads to 1,4-dihydroxynaphthalene without a significant impurity of *para*-quinone, supposedly because of the reduced oxygen content as compared with heating at 50 °C.

§§ 2,5-Dihydroxybenzoic acid was used as a matrix.



L = AcOH, Cat = $APMn^{3+}$(L), counter ion is not shown

Scheme 1

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