

Catalytic oxidation reactions of aromatic diamines by transition metal complexes

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Abstract

The catalytic reactions of M(TPP)Cl (M = Fe (**1**), Mn (**2**)), Fe(TMP)Cl (**3**), and Fe(TDCPP)Cl (**4**) (H₂TPP = 5,10,15,20-tetraphenylporphyrin; H₂TMP = 5,10,15,20-tetramesitylporphyrin; H₂TDCPP = 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin) with 2,4-diaminotoluene (**5**) and *p*-phenylenediamine (**6**) were carried out using *t*-BuOOH (3 M isooctane solution) as oxidant. With the former substrate, the nitro derivatives 2-amino-4-nitrotoluene (**5a**) and 2,4-dinitrotoluene (**5b**) (total yield of **5a** + **5b** ranges between 27–55%) were obtained with low yields and their amounts depend on the catalyst used. An other oxidation product of **5** was 3-amino-4(*tert*-butyldioxy)-4-methyl-2,5-cyclohexadien-1-imine hydrochloride (**5c**) (20%). In the oxidation reaction of **6**, 4-nitroaniline (**6a**) (11%) was obtained only with catalyst **1**, being an unidentified black solid (**6b**) the major oxidation product. **6b** was always the main product with all the studied catalysts (**1–3**), while the yields and nature of the recovered azobenzenes depend on the metalloporphyrin used: the highest yield of 4,4'-dinitroazobenzene (**6c**) (37%) was obtained with **3** in the presence of acetic acid, 4,4'-diaminoazobenzene (**6d**) (19%) was obtained with **4**, and 4-amino,4'-nitroazobenzene (**6e**) (17%) with **3**. The catalytic reactions of Mo(O)(O₂)₂(H₂O)(HMPA) (**7**) (HMPA = hexamethylphosphotriamide), with **5**, **6**, and 4-aminodiphenylamine (**8**), in the presence of H₂O₂ (35% w/w water solution) as oxidant, were studied. The corresponding mononitro derivatives, **5a**, **6a**, and 4-nitrodiphenylamine (**8a**) were obtained with fair selectivity (35, 70, and 60%, respectively).

Keywords: Catalytic oxidation; Aromatic diamines; Mn; Fe-tetraarylporphyrins; Mo(VI) peroxo complex

1. Introduction

Following our investigations in the field of selective oxidation reactions of amines catalysed by metal complexes [1], we report here a study on the oxidation of aromatic diamines.

Metal catalysed systems have been widely used to obtain oxygenated products of amines [2–6], but only in few cases were they applied to diamines [7]. Due to the low values of diamine reduction potentials [8], a very broad number of oxidation reactions are expected; indeed, these molecules are currently used as antioxidants or antiozonants, giving polymeric compounds as main products [8]. The aim of this study was to

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find out simple and selective oxidation reactions by interaction with metal centres.

Because of our previous experiences [1], we firstly studied the reaction of 2,4-diaminotoluene (**5**) and *p*-phenylenediamine (**6**) with *t*-BuOOH, in the presence of the metalloporphyrin complexes M(TPP)Cl (**1–2**) (M = Fe, Mn), Fe(TMP)Cl (**3**) and Fe(TDCPP)Cl (**4**). These catalytic systems showed poor selectivities in nitrogen-oxidised products (mono-, di-nitro- and azo-derivatives), but the identification of the interesting adduct (**5c**) allows us to speculate that at least three mechanisms can be operative in these reactions (*electron-transfer and oxygen-transfer via intermediate metallo-oxo species* [9,10] and *ligand-transfer via metalloporphyrin–OOBu' adduct* [11]) giving a deeper insight on metalloporphyrin catalysed oxygenations.

The oxidation reactions of **5**, **6** and 4-aminodiphenylamine (**8**) were then developed by using a molybdenum(VI) complex, Mo(O)(O₂)₂(H₂O)(HMPA) (**7**) well known for its ability to transfer an oxygen atom to olefins [3] and to aromatic amines [4] in the presence of H₂O₂, as oxidant. This catalytic system afforded higher yields of mononitro derivatives than those obtained with metalloporphyrins.

2. Experimental

All reaction were carried out with magnetic stirring at room temperature either under aerobic or anaerobic conditions, as specified in the experimental section. CH₂Cl₂ and CH₃CN, Baker Analyzed reagents, were used as received, unless otherwise stated. The starting complexes, Mo(O)(O₂)₂(H₂O)(HMPA) [12], Fe(TPP)Cl, Mn(TPP)Cl, Fe(TMP)Cl, and Fe(TDCPP)Cl were prepared as described in the literature [13]. *Tert*-butylhydroperoxide (3 M solution in isooctane, Aldrich) and H₂O₂ (35% w/w water solution, Merck) were used as received. The diamines (4-aminodiphenylamine, 2,4-diaminotoluene, *p*-phenylenediamine) were

purchased by Aldrich and used after crystallisation and stored under nitrogen.

Infrared spectra were recorded in nujol on a FT-IR BioRad FTS-7. ¹H and ¹³C NMR spectra were recorded on a Bruker WP-80SY and AC 300 spectrometers. Elemental analyses were carried out on a Perkin-Elmer 2400 CHN Elemental Analyzer in the Analytical Laboratories of Milan University. The chloride analysis was performed with a Perkin-Elmer 250 HPLC, equipped with a 0.15 m (Ø = 4.6 mm) Alltech Anion HC column, coupled with an Alltech 350 conductivity detector. GC analyses were performed using a Hewlett Packard 5890 gas chromatograph equipped with a 30 m HP5 capillary column (Ø = 0.53 mm). HPLC analyses were carried out on Hewlett Packard 1050 instrument. Mass spectra were recorded on VG 7070 EQ instrument (NBA = nitrobenzylalcohol as matrix). Stock CH₂Cl₂ solutions (1 × 10⁻³ M) of the metalloporphyrin complexes (**1–4**) were prepared in 20 mL volumetric flasks.

2.1. General procedure of the reactions of 2,4-diaminotoluene (**5**) with metalloporphyrin complexes (**1**, **3** and **4**)

To a solution of the appropriate metalloporphyrins (1 mL of the 10⁻³ M stock solutions, 10⁻³ mmol) in CH₂Cl₂ (100 mL), 1-methylimidazole (16.4 mg, 0.2 mmol) and 2,4-diaminotoluene (**5**) (122 mg, 1 mmol) were added under aerobic conditions. After dissolution of **5** the desired amount of *t*-BuOOH (3 mL of a 3 M isooctane solution, 9 mmol) was added. The colour of the solution quickly turns from brown–yellow to brick-red. After one or two hours, samples were withdrawn, washed with a saturated aqueous solution of Na₂S₂O₃ · 5H₂O (weakly basic by addition of a small amount of sodium carbonate), dried on calcium sulfate, and analysed by GC (Table 1). After 24 h of reaction the brick-red precipitate **5c** was filtered off and washed with CH₂Cl₂. The mother liquors were treated as above described, and analysed by gas chromatography (C₆H₅NO₂ internal

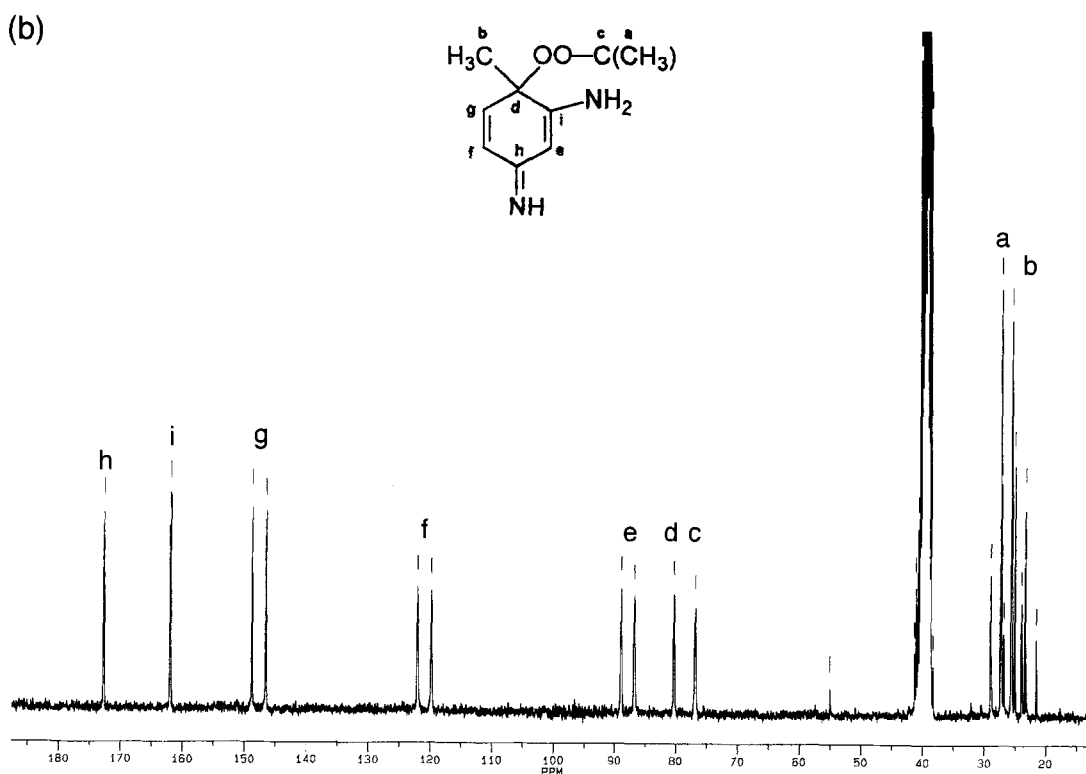
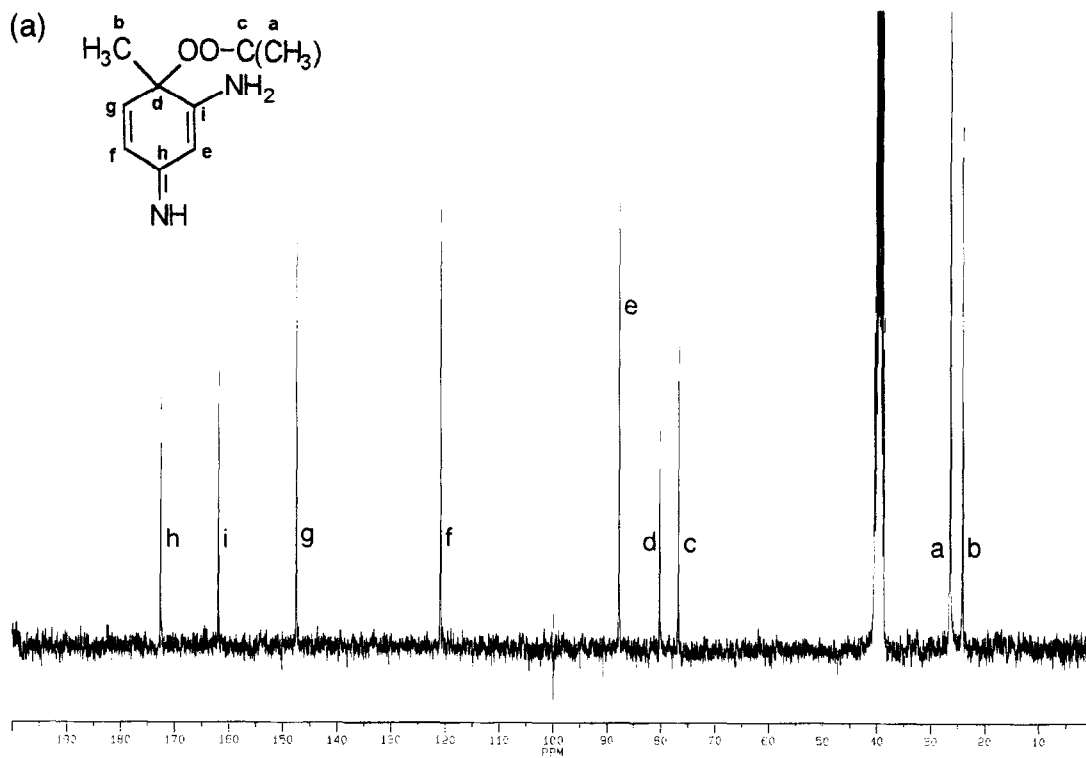


Fig. 1. (a) ^{13}C NMR of **5c** in $\text{DMSO-}d_6$ (totally decoupled). (b) ^{13}C NMR of **5c** in $\text{DMSO-}d_6$.

Table 1
Oxidation^a of **5**

#	Time (h)	Catalyst (mmol)	Ligand (%)	Yields (%)		Conv.
				5a ^b	5b ^b	
I	1	Fe(TPP)Cl	—	46.0	7.4	98
II	1	Fe(TPP)Cl	0.2	42.0	13.0	100
III	2	Fe(TMP)Cl	—	46.0	4.6	100
IV	2	Fe(TMP)Cl	0.2	50.0	3.8	100
V	1	Fe(TDCPP)Cl	—	22.0	5.0	100
VI	1	Fe(TDCPP)Cl	0.2	26.0	1.8	98

^a Reaction conditions: **5** 1×10^{-2} M (1 mmol), catalyst 1×10^{-5} M (1×10^{-3} mmol), *t*-BuOOH 9×10^{-2} M (9 mmol), CH₂Cl₂ (100 mL), RT.





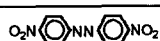
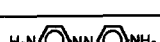
^b Determined by GC.

standard) and recognized by comparison with authentic samples. The yields are reported in Table 1.

2.2. 3-amino-4(*tert*-butyldioxy)-4-methyl-2,5-cyclohexadien-1-imine hydrochloride (**5c**)

The brick red compound (**5c**) (48–55 mg; 20–23%) was obtained as precipitate in all the reactions of **5** with the iron porphyrins **1**, **3** and **4**. Mp = 192–193°C (dec.). ¹H NMR (DMSO-*d*₆, ppm): 1.15 (s, 9 H); 1.40 (s, 3 H); 5.18 (bs, 1 H); 6.45 (dd, 1 H, *J*_{H-H} = 9.9 Hz); 6.75 (dd, 1 H, *J*_{H-H} = 9.9 Hz); 8.25 (bs, 1 H, D₂O exchange); 9.30 (bs, 2 H, D₂O exchange); 9.50 (bs, 1 H, D₂O exchange). ¹³C NMR (DMSO-*d*₆, ppm): 24.08 (q); 26.32 (q); 76.75 (s); 80.23 (s); 87.73 (d); 120.85 (d); 147.57 (d); 161.94 (s); 172.64 (s) (see Fig. 1a and b). Elemental analysis: C, 50.8; H, 6.6; N, 11.4; Cl, 14.8. Calcd. for C₁₁H₁₉ClN₂O₂: C, 53.5; H, 7.7; N,

Table 2
Oxidation^a of **6**

#	time (h)	CATALYST	tBuOOH (mmol)	LIGAND (mmol)	PRODUCTS	SELECTIVITY ^b %
I	0.5	Fe(TPP)Cl	3	0.2	 6a	10.9
					 6c	2.9
					black solid 6b	18.0 ^c
II	36	Fe(TMP)Cl	3	0.2	 6c	3.7
					 6e	17.0
					black solid 6b	43.0 ^c
III	36	Fe(TMP)Cl	9	- ^d	 6c	37.0
					black solid 6b	55.0
IV	2	Mn(TPP)Cl	3	0.2	 6d	19.0
					black solid 6b	22.0

^a Reaction conditions: **6** 1×10^{-2} M (1 mmol), catalyst 1×10^{-5} M (1×10^{-3} mmol), CH₂Cl₂ (100 mL), RT.

^b Conversion always 100%.

^c The selectivity percentages for 'black solid' are in % w/w.

^d CH₃COOH (0.5 mmol).

11.4; O, 12.3; Cl, 14.4. $\Lambda_M = 49 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ($\text{C}_2\text{H}_5\text{OH}$, 25°C). FAB⁺/MS (NBA): 211 (MH^+); 154 ($\text{MH-}t\text{-Bu}^+$); 138 ($\text{MH-}t\text{-BuO}^+$); 122 ($\text{MH-}t\text{-BuOO}^+$).

IR (nujol, cm^{-1}): $\nu(\text{NH}_2 + \text{NH}_3^+)$: 3295 (br) and 3089 (br); $\nu(\text{C}=\text{C})$: 1667; $\nu(\text{C}=\text{N})$: 1533; $\nu(\text{O}-\text{O})$: 1182.

2.3. General procedure of the reactions of *p*-phenylenediamine (**6**) with metalloporphyrin complexes (**1–3**)

To a solution of the appropriate metalloporphyrins (1 mL of the 10^{-3} M stock solution, 10^{-3} mmol) in CH_2Cl_2 (100 mL), 1-methylimidazole (16.4 mg, 0.2 mmol) and *p*-phenylenediamine **6** (108 mg, 1 mmol) were added, under dinitrogen. After dissolution of **6**, the desired amount of *t*-BuOOH (1 or 3 mL of a 3 M isooctane solution, 3 or 9 mmol) was added. The colour of the solution quickly turns from brown–yellow to orange. After the complete conversion of the diamine (different times depending on the metalloporphyrin and the molar equivalents of *t*-BuOOH used) the black precipitate **6b**, was filtered off and washed with CH_2Cl_2 . To eliminate the excess of the oxidant, the mother liquors were treated with a water solution of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ (0.2 M), weakly basic by addition of a small amount of sodium carbonate. The organic solution was separated, dried on calcium sulfate and evaporated to dryness. The organic products, **6a**, **6c** and **6e**, were purified, by flash chromatography on silica ($\text{CH}_2\text{Cl}_2/\text{hexane}$) (Table 2).

4-nitroaniline (**6a**) was obtained following the general procedure using Fe(TPP)Cl as catalyst, 3 molar equivalents of *t*-BuOOH and 0.5 h of reaction time. The yellow–orange residue of the reaction was chromatographed on silica ($\text{CH}_2\text{Cl}_2/\text{hexane} = 6/4$) obtaining **6c** (4 mg, 2.9%) and the lemon-yellow solid **6a** (15 mg, 10.9%); mp 146°C (149°C [14]). ^1H NMR (CDCl_3 , ppm): 4.4 (bs, 2 H, D_2O exchange); 6.62 (d, 2 H); 8.07 (d, 2 H).

Black solid (**6b**) was the precipitate obtained

in all the reactions of **6** with the metalloporphyrins **1–3** (25–60 mg, 18–43% w/w). Mp $> 300^\circ\text{C}$. Elemental analysis: C, 50.2; H, 5.68; N, 19.6. It contains chloride ions and behaves as an electrolyte in H_2O . IR (nujol, cm^{-1}) $\nu(\text{NH}_2 + \text{NH}_3^+)$: 3328 (br), 3201 (br) and 3161 (br); $\nu(\text{C}=\text{C})$: 1599; $\nu(\text{C}=\text{N})$: 1513. ^1H NMR (D_2O , ppm): 1.26 (s), 2.24 (s), 7.13 (s).

4,4'-dinitroazobenzene (**6c**) (E-form); following the general procedure: (i) with Fe(TPP)Cl, 3 molar equivalents of *t*-BuOOH, 0.5 h of reaction time, **6c** (4 mg; 2.9%) was obtained in mixture with **6a**; (ii) with Fe(TMP)Cl, 3 molar equivalents of *t*-BuOOH, 36 h of reaction time, **6c** (5 mg; 3.7%), was obtained in mixture with **6e**. The title compound was obtained as unique soluble product by using Fe(TMP)Cl as catalyst, 9 molar equivalents of *t*-BuOOH, 36 h of reaction time, in the presence of CH_3COOH (0.5 molar equivalents with respect to **6**). In this case the deep-orange mother liquors were evaporated to dryness obtaining the orange–red **6c**. (50 mg, 37%). Mp 225°C (222°C [14]). ^1H NMR (CDCl_3 , ppm): 8.11 (d, 4 H); 8.44 (d, 4 H). CI/MS: 272 (M^+), 150 ($\text{M}-\text{C}_6\text{H}_4\text{NO}_2$)⁺, 122 ($\text{C}_6\text{H}_4\text{NO}_2$)⁺.

4,4'-diaminoazobenzene (**6d**) was obtained after 2 h, following the general procedure using Mn(TPP)Cl as catalyst and 3 molar equivalents of *t*-BuOOH. The yellow mother liquors evaporated to dryness yielded the golden-yellow solid **6d** (20 mg; 19%). Mp 245°C (250°C [14]). ^1H NMR (CDCl_3 , ppm): 3.92 (bs, 4 H, D_2O exchange), 6.74 (d, 4 H); 7.75 (d, 4 H); CI/MS: 212 (M^+), 120 ($\text{M}-\text{C}_6\text{H}_4\text{NH}_2$)⁺, 92 ($\text{C}_6\text{H}_4\text{NH}_2$)⁺.

4-amino, *4'*-nitroazobenzene (**6e**) was obtained following the general procedure using Fe(TMP)Cl, 3 molar equivalents of *t*-BuOOH and 36 h of reaction time. The deep-orange residue was chromatographed on silica ($\text{CH}_2\text{Cl}_2/\text{hexane} = 8/2$) obtaining **6c** (5 mg, 3.7%) and the orange solid **6e** (20 mg, 17%). Mp 210°C (216°C [14]). ^1H NMR (CDCl_3 , ppm): 4.2 (bs, 2 H, D_2O exchange); 6.75 (d, 2 H); 7.85 (d, 2 H); 7.98 (d, 2 H); 8.34 (d, 2 H).

CI/MS: 242 (M^+), 150 ($M-C_6H_4NH_2$)⁺, 122 ($C_6H_4NO_2$)⁺, 92 ($C_6H_4NH_2$)⁺.

2.4. Reaction of $Mo(O)(O_2)_2(H_2O)(HMPA)$ (**7**) with 2,4-diaminotoluene (**5**)

To the yellow solution of $Mo(O)(O_2)_2(H_2O)(HMPA)$ (**7**) (37.3 mg, 0.1 mmol) in CH_3CN (5 mL) 2,4-diaminotoluene (**5**) (122 mg, 1 mmol) and H_2O_2 (0.43 mL of a 35% w/w water solution, 5 mmol) were added under nitrogen. After 5 h, the complete consumption of the amine **5** was observed and the yellow solution was analysed by HPLC (CH_3CN 65%, H_2O 35%; naphthalene as internal standard), obtaining a selectivity of 35% in the mono nitro derivative **5a**. Its identity was confirmed by comparison with an authentic sample.

2.5. Reaction of $Mo(O)(O_2)_2(H_2O)(HMPA)$ (**7**) with *p*-phenylenediamine (**6**)

To the yellow solution of **7** (37.3 mg, 0.1 mmol) in CH_2Cl_2 (or in CH_3CN) (5 mL) *p*-phenylenediamine (**6**) (108 mg, 1 mmol) and H_2O_2 (0.43 mL of a 35% w/w water solution, 5 mmol) were added under nitrogen. The colour of the solution became red and after 6 h the conversion of the amine was complete. HPLC analyses (CH_3CN 65%, H_2O 35%; naphthalene internal standard) showed a selectivity of 91.5% in the corresponding mono nitro derivative **6a**. After decomposition of the excess of H_2O_2 as previously described, **6a** was purified by flash chromatography using a mixture toluene–methanol (9:1) as eluant (96 mg; 70%).

2.6. Reaction of $Mo(O)(O_2)_2(H_2O)(HMPA)$ (**7**) with 4-aminodiphenylamine (**8**)

To the yellow solution of **7** (37.3 mg, 0.1 mmol) in CH_2Cl_2 (5 mL) 4-aminodiphenylamine (**8**) (184 mg, 1 mmol) and H_2O_2 (0.43 mL of 35% w/w water solution, 5 mmol) were added under nitrogen. HPLC analyses (CH_3CN 65%, H_2O 35%; naphthalene as internal stan-

dard) carried out after 21 h showed the total conversion of the amine **8** and the selectivity of 67.3% in the corresponding 4-nitrodiphenylamine (**8a**). After decomposition of the excess of H_2O_2 , the yellow solution was evaporated to dryness and purified by flash chromatography on silica (CH_2Cl_2). The yellow crystalline compound **8a** was obtained (128 mg; 60%). Mp = 132°C (130°C [15]). IR (nujol, cm^{-1}): $\nu(NH)$ = 3341 (br); $\nu(NO_2)$ = 1540 and 1328; $\delta(NH)$ = 1584. CI/MS: 214 (M^+), 198($M-O$)⁺, 184($M-NO$)⁺, 168($M-NO_2$)⁺. Its identity was confirmed by comparison with an authentic sample [15].

3. Results and discussion

3.1. Reactions of metalloporphyrins with 2,4-diaminotoluene (**5**)

The catalytic reactions of **5** with metalloporphyrins ($M(P)Cl$) **1**, **3** and **4** were carried out in CH_2Cl_2 at room temperature in the presence of *t*-BuOOH as oxidant, obtaining **5a**, **5b**, and **5c**, as depicted in Fig. 2.

The molar ratios were catalyst/**5**/1-methylimidazole/oxidant = 1/1000/0 (or 200)/9000 (i.e., nine molar equivalents of oxidant with respect to the diamine). After 24 h the compound **5c** was obtained as brick-red precipitate (ca. 20%) by using any catalyst, while the

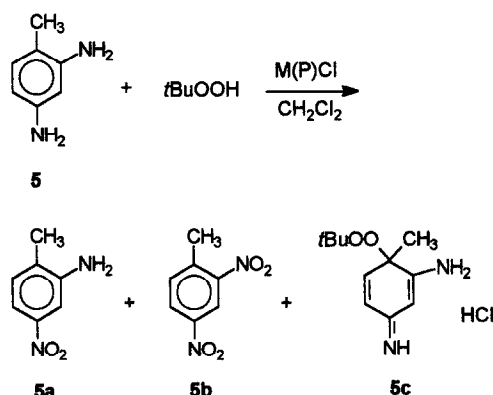


Fig. 2.

amounts of **5a** and **5b** in solution were determined by GC analyses (after 1 and 24 h, Table 1). Together with these two products the gaschromatographic spectra revealed the presence of an unknown compound detected only in the early stages of the reaction. GC-MS analysis showed that it could be the intermediate 4-nitroso-2-aminotoluene, which we were never able to isolate by chromatography. The total amount of the nitro derivatives depends on the metal complex used, being the electron-rich catalyst **1** and **3** (ca. 50%) more active than **4** (ca. 27%). Higher oxidant/substrate ratios did not increase the overall yields of **5a** and **5b**, neither their relative ratio, thus indicating that the oxidation rate of the mono nitro derivative **5a** to the dinitro **5b** is extremely low; in fact a blank experiment, carried out with **5a** as substrate, under the above reported conditions, did not yield **5b**.

It must be pointed out that, in all the studied reactions, the mass balance was lower than the theoretically expected value, probably due to the formation of soluble polymeric compounds, which are not detectable by GC and cannot be recovered through a silica gel column.

When three equivalents (50% of the stoichiometric value) of *t*-BuOOH were used, with catalyst **3** some unreacted diamine **5** was detected together with lower amounts of **5a** and **5b**; interestingly, in this case, the molar ratio **5a**/**5b** was comparable to the one obtained in the presence of nine equivalents of *t*-BuOOH. This last result, coupled with the experimental evidence that **5a** is insignificantly converted to **5b**, indicates that two different reaction pathways occur for the formation of mononitro and dinitro compounds.

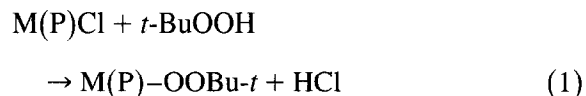
In preliminary experiments we studied the influence of the metal nature (Fe or Mn) on the catalytic efficiency. The iron complex **1** was found largely more active than the analogous manganese, thus no other manganese complexes have been further investigated with diamine **5**.

The influence of the axial ligand on the catalytic activity of **1**, **3** and **4** was studied,

carrying out the reaction with 20% of 1-methylimidazole with respect to the diamine **5**. Its presence substantially did not modify conversions and selectivities of nitro compounds (Table 1).

The characterisation of the insoluble compound **5c** needed a series of analytical data (see Experimental). ¹³C NMR unambiguously indicates the presence of nine different carbon atoms and their assignments are reported in Fig. 1a and b. ¹H NMR showed the expected signals for the C–H protons of **5c**, while a strange set of peaks for N–H groups was found. Three chemical shifts (8.25, 9.30, 9.50 ppm) of intensity 1:2:1 can be explained by the presence of an HCl proton simultaneously hydrogen-bonded to the imino and the amine groups. FAB⁺/MS analysis strongly confirms the proposed structure of **5c**, featuring the OOBu' group.

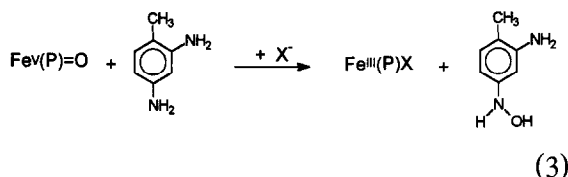
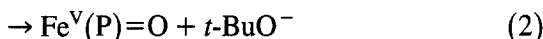
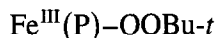
The ionic nature of **5c** was confirmed by conductivity measurements in EtOH ($\Lambda_M = 49 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$, 25°C). The obtained chloride salt can arise from HCl generated by coordination of *t*-BuOOH to the metal centre (Eq. (1)):



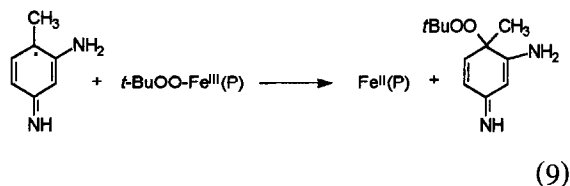
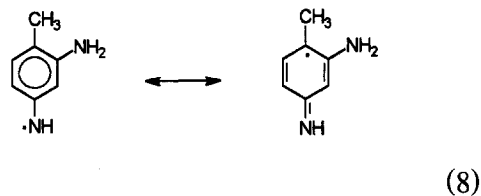
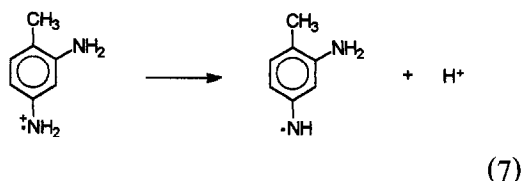
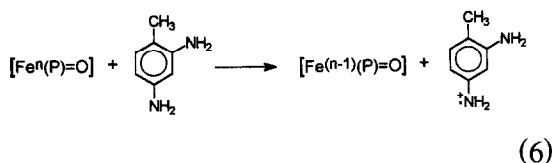
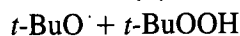
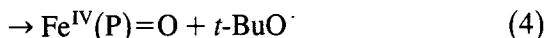
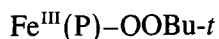
but the amount of chlorine derived by M(P)Cl (10^{-3} mmol) cannot afford the large quantity found of **5c** (0.2 mmol). Thus most likely HCl comes out by solvent oxidation and, although we were unable to understand the fate of the oxidised methylene chloride, we noticed the presence of low boiling polychlorinated compounds in solution, as ascertained by GC-MS analyses.

In order to explain the presence of **5c**, which contains one *t*-BuOO group, and to understand why the yields of **5a** and **5b** increased, using the electron-rich catalysts **1** and **3**, with respect to **4**, we considered that two mechanisms could be operative: (i) oxygen-transfer from iron(V)–oxo species, and (ii) electron-transfer from the diamine to a high valent iron–oxo intermediate to form an aniline radical cation.

(i) When the heterolytic scission of the O–O bond takes place, $\text{Fe}^{\text{V}}(\text{P})=\text{O}$ is generated (Eq. (2)) [10], as previously observed also for manganese oxo complexes [9], [16]; the electrophilic oxygen can be transferred to the diamine, according to the well known behaviour of the electrophilic oxygen of the oxo diperoxo molybdenum complex **7** (reported later), giving a mono hydroxylamine intermediate (Eq. (3)), which can be easily oxidised to the products **5a** and **5b**.



(ii) Electron-transfer (Eq. (6)) can occur from the diamine to both metallo–oxo species (of iron(IV) and (V)) derived by homolytic (Eq. (4)) or heterolytic (Eq. (2)) cleavage of the O–O bond in the (P)Fe–OOBu^t adduct. The aniline radical cation thus obtained, easily undergoes proton shift giving a nitrogen radical (Eq. (7)) that could: (i) react with diamine giving rise to a polymeric reaction; or (ii) undergo OOBu^t ligand-transfer, as already reported for manganese [11], from the (P)Fe–OOBu^t adduct to the carbon centred radical, being this last stabilised by resonance (Eq. (8)), producing **5c** (Eq. (9)).



The obtained results do not exclude, however, possible electron and/or hydrogen transfer mechanisms due to the radical intermediates ($t\text{-BuO}^\cdot$ and $t\text{-BuOO}^\cdot$, see Eqs. (4) and (5)), derived from the decomposition of the oxidant.

The different capability of the catalysts **1**, **3** and **4** to yield the nitro and dinitro derivatives **5a** and **5b**, can be explained considering the electronic effects of the substituents on the *meso* phenyl rings. A higher extent of E.T. (i.e. lower amounts of nitro derivatives) showed by $\text{Fe}(\text{TDCPP})\text{Cl}$, **4**, with respect to **1** and **3**, can be rationalised by two hypothesis: (a) being **4** the most electron-deficient catalyst, it favours the homolytic scission of the O–O bond [17], thus generating (P)Fe^{IV}=O in spite of (P)Fe^V=O; (b) if only the heterolytic cleavage occurs, giving (P)Fe^V=O species, as reported by Traylor et al. [10], the explanation for the large E.T. can be found in the formation of a favoured transition state, characterised by a high charge separation, which is accomplished by a highly positive iron centre.

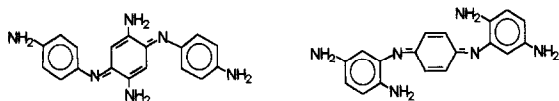


Fig. 3.

3.2. Reactions of metalloporphyrins with *p*-phenylenediamine (**6**)

The catalytic reactions of the metalloporphyrins **1–3** with **6** were initially carried out under the same conditions reported in the case of **5** (catalyst/**6**/1-methylimidazole/oxidant = 1/1000/0/9000). After 36 h of reaction a large amount (ca. 43% w/w) of a black precipitate **6b** was recovered after filtration. Although it is well known that **6** gives polymeric compounds (aniline blacks) and two trimeric forms are reported (Bandrowski's base and its isomer; Fig. 3) [8] under oxidative conditions, many attempts (elemental analyses, ¹H NMR in D₂O or DMSO, conductivity, IR, FAB⁺/MS) aimed to characterise the poorly soluble compound **6b**, were carried out, but unsuccessfully.

Therefore, we decided to lower the amount of oxidant (3 molar equivalents), to minimise the overoxidation products, and to add the axial ligand because we found that the oxidation of **6** gave higher amounts of soluble products.

Thus by using catalyst/**6**/ligand /oxidant = 1/1000/200/3000 molar ratios, the amount of the black precipitate **6b** lowered and a variety of azo-compounds were obtained in low yields, depending of the used metalloporphyrins (Table 2).

The comparison between the catalytic activity of Mn and Fe porphyrins was carried out using catalysts **1** and **2**. The reaction of Mn(TPP)Cl with **6** yielded 19% of 4,4'-diaminoazobenzene **6d** (entry IV), while the use of Fe(TPP)Cl afforded a mixture of 4-nitroaniline **6a** and 4,4'-dinitroazobenzene **6c** (11% and 3% respectively, entry I). The trend, previously found with diamine **5**, is followed also in this case, being the iron complex most suitable for the oxygen transfer.

The reaction of Fe(TMP)Cl with **6** yielded a mixture of 4-amino,4'-nitroazobenzene **6e** (17%) and 4,4'-dinitroazobenzene **6c** (3.7%) (entry II), but the same reaction carried out in the presence of CH₃COOH (catalyst/**6**/oxidant/acetic acid = 1/1000/9000/500) gave the highest amount of 4,4'-dinitroazobenzene (50 mg; 37%) (entry III). This experiment was dictated by the knowledge that in acid catalysed oxidation reactions, the coupling between a nitroso intermediate and the unreacted amine is unfavoured [18]. The larger amount of **6c** obtained under acidic conditions, suggests that the formation of the azo compounds does not occur through a nitroso intermediate and our explanation for the formation of these compounds involves again the existence of two mechanisms, as previously illustrated for diamine **5** (electron transfer and oxygen transfer). The electron transfer could be responsible of the formation of 4,4'-diaminoazobenzene [6], while the oxygen transfer could be responsible of the further oxidation of the amino groups to mono nitro or dinitro derivatives.

3.3. Reactions of Mo(O)(O₂)₂(HMPA)(H₂O) (**7**) with diamines **5**, **6** and **8**

To confirm the hypothesis that the nitro-containing products **5a**, **5b**, **6 (a, c, e)** were formed by transfer of an electrophilic oxygen atom from the metalloporphyrin catalysts, we decided to compare the catalytic oxidation reactions of **5**, **6** and **8** carried out in the presence of **7**.

It has been reported that the oxo peroxy complex of molybdenum(VI), oxo(*N*-phenylhydroxylamido-O,N) (pyridine-2,6-dicarboxylato) (hexamethylphosphotriamide) molybdenum(VI), (Mo(dipic)(O)(O₂)(HMPA)), catalyses the oxidation of substituted anilines to the corresponding nitroso derivatives [5]; the proposed mechanism indicates the nucleophilic attack of the amine onto the electrophilic peroxide oxygen; in the second step, this oxygen atom is transferred, affording a nitroso compound.

The reactions of **7** (a complex similar to that

used by Moller and Jorgensen [5]) with **5**, **6** and **8** were carried out at room temperature and under nitrogen, using H₂O₂ as oxidant and the following molar ratios: catalyst/amine/oxidant = 1/10/50. The diamines **5** and **6** were converted, in 6 h, to the corresponding mono nitro anilines **5a** (35%) and **6a** (70%), while 4-aminodiphenylamine (**8**) was converted, in 24 h to 4-nitro-diphenylamine (**8a**, 60%). At this stage of our research, only compounds **5a**, **6a** and **8a** were recovered and quantified and the fate of the metal complex **7** was not investigated.

4. Conclusions

The oxidation reactions of the studied aromatic diamines can follow two different pathways; the electron transfer does not give selective reactions, while the transfer of an electrophilic oxygen atom affords nitro compounds. The metalloporphyrin complexes are more reactive but less selective with respect to molybdenum(VI) complex; indeed the electron transfer cannot be excluded since metalloporphyrin are characterised by high reduction potentials, while the molybdenum(VI) complex behaving as an organic peracid, results in better selectivities of mono nitro compounds.

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