

# $\text{FeCl}_2\text{py}_4^+$ catalyzed transformation of aromatic amines by HOOH under mild conditions

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## Abstract

$\text{FeCl}_2\text{py}_4^+$  is capable of activating HOOH for the selective and efficient (yields range roughly from 50 to 80%) transformation of anilines at *room temperature* using pyridine as the solvent. Initially, aniline yields mainly nitrosobenzene that in turn reacts with more aniline to form the corresponding azo and azoxybenzene derivatives. Replacing HOOH by *t*-BuOOH in the system, changes the product distribution dramatically forming only nitrobenzene. Under the same conditions  $\text{FeCl}_2\text{py}_4^+$  efficiently catalyzes the mono-demethylation of *N,N'*-dimethylaniline by HOOH. © 1999 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

The selective transformation of aniline represents an important class of reactions as pointed out in recent publications [1–9] because of its relevance to the industrial [10–13], biological [14–16] and environmental world [17,18]. From an industrial point of view, aromatic nitroso compounds are of interest because of their applications in the vulcanization of rubber, the stabilization of halogenated materials and as antioxidants in lubrication oil [10,11].

Several methods for the transformation of aniline have been reported in the literature, both stoichiometric [4–6,19–24] and catalyzed by transition metal compounds [2,3,7–9,25–29].

Oxidants such as  $\text{FeO}_4^{2-}$  transform anilines into nitrobenzene or azobenzene depending on the pH of the reaction [4], whereas in aprotic solvents they form azobenzene [5,6]. Classical oxidants such as  $\text{MnO}_2$  are used in order to obtain azobenzene [19]. Aqueous peracids oxidize *ortho*-substituted anilines to nitrobenzene [20] and nonsubstituted anilines to azo- and azoxybenzene [21] while anhydric peracids oxidize even unsubstituted aniline to nitrobenzene [22] or nitrosobenzene [23] depending on the reaction conditions.

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The use of molecular oxygen to activate transition metal complexes for the oxidation of aniline is still a major challenge in this field. Only the oxidation of activated substituted anilines has been achieved using cuprous chloride as catalyst to form aza derivatives [29].

*t*-BuOOH has been used more successfully as oxidant for the catalytic oxidation of aniline in the presence of transition metal compounds both in a homogeneous and heterogeneous fashion. Generally, in both cases the main product formed is nitrobenzene with high selectivities [2,3,25, 26].

Hydrogen peroxide, being cheaper and non-polluting, is a much more attractive oxidant. The oxidation of *p*-chloroaniline to dichloroazobenzene with HOOH-boric acid at 50°C has been reported [24]. Transition metal catalyzed oxidations of anilines with HOOH have been performed in a homogeneous [7,27,28] and also in a heterogeneous manner [8,9]. The latter suffer from either use of high temperatures [8] or long reaction times and poor efficiencies with regard to HOOH [9].

Several reports have been presented in the literature describing the use of HOOH for the oxidation of aniline in a homogeneous phase. In this sense, RuCl<sub>3</sub> has been reported to catalyze [28] the transformation of aniline into nitro- and azoxybenzene although it needs high reaction time (24 h) and temperature (90°C). A Mo catalyst has been recently reported to selectively oxidize anilines to the corresponding nitrosobenzenes at room temperature but it needs 14–72 h to proceed and the efficiency with regard to HOOH is low [7]. Another catalytic system has been described at low temperature (14°C) that uses a W catalyst to transform anilines mainly into nitroso and azoxybenzene derivatives although it suffers from very long reaction time (6–20 days) and low selectivity [27].

Given the currently severe and strict environmental and industrial demands we decided to search for a catalyst that could transform aniline selectively and efficiently to nitrosobenzene and that necessarily had to work fast at room tem-

perature and use the cheap and nonpolluting HOOH as oxidant.

We report here on the characterization of an FeCl<sub>2</sub>py<sub>4</sub><sup>+</sup> based catalytic system that constitutes the first example of a system complying with all the requirements stated above.

## 2. Experimental

### 2.1. Equipment

The reaction products were separated and identified with a Hewlett-Packard 5880A Series gas chromatograph equipped with an HP-1 capillary column (cross-linked methyl-silicone-gum phase, 12 m × 0.2 mm i.d.) or a Shimadzu GC-17A equipped with a Trb-5 capillary column (30 m × 0.25 mm i.d.) and by gas chromatography–mass spectrometry (Hewlett-Packard 5790A Series gas chromatograph with a mass-selective detector).

Cyclic voltammetric experiments were performed in a PAR 263A EG&G potentiostat using a three electrode cell. Glassy carbon disk electrodes (1.5 mm diameter) from BAS were used as working electrode, platinum wire as auxiliary and SSCE as the reference electrode. All cyclic voltammograms presented were recorded at 100 mV/s scan rate under either nitrogen or argon atmosphere. The complexes were dissolved in previously degassed pyridine as the solvent, containing the necessary amount of (*n*-Bu)<sub>4</sub>NPF<sub>6</sub> to yield a 0.1 M ionic strength solution. The concentration of the complexes were always 5 mM.

Electrospray ionization mass spectra were acquired using a Navigator quadrupole instrument (MassLab Group, Finnigan, Manchester, UK) with a MassLab 2.0 data system and DEC Venturis FX for data processing. The samples were introduced via liquid chromatographic pump (Gynkotek, Germering, G) at a flow rate of 50 μl/min using methanol as the mobile phase. The drying gas flow rate was kept at 200 l/h,

source temperature at 120°C and the voltage needle was 3.5 kV. The cone voltage was optimized at 50 V. Positive ion spectra were acquired in full scan 100–1200  $m/z$  at 5 s/scan in continuum mode.

## 2.2. Chemicals and reagents

The reagents for the investigations were of the highest purity commercially available and were used without further purification. Burdick and Jackson ‘distilled in glass’ grade pyridine (py, 0.007% H<sub>2</sub>O), acetonitrile (MeCN, 0.002% H<sub>2</sub>O) and glacial acetic acid (HOAc, ACS grade, Fischer) were used as solvents. [FeCl<sub>2</sub>py<sub>4</sub>]Cl is obtained in situ upon dissolving hexahydrated iron trichloride [Fe(Cl)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>]Cl · 2H<sub>2</sub>O [30] from Aldrich in pyridine. [FeCl<sub>2</sub>py<sub>4</sub>] is obtained when FeCl<sub>2</sub> (Aldrich) is dissolved in pyridine under an inert atmosphere of nitrogen or argon [31]. The other Fe and Co metal complexes were prepared according to previously published procedures [32] and were allowed to re-

main in vacuum for 24 h over CaSO<sub>4</sub> prior to use.

## 2.3. Methods

The investigation of the HOOH and *t*-BuOOH activation by the transition metal compounds (5 mM) used 7 ml solutions that contained 1 M substrate in the appropriate solvent mixture. Hydrogen peroxide (30% in water) or *t*-BuOOH (5.5 M in 2,2,4-trimethylpentane) was injected to give 100 mM peroxide. After the desired reaction time under constant stirring at room temperature (24 ± 2°C) under Ar or O<sub>2</sub> (1 atm), samples of the reaction solution were injected into a capillary-column gas chromatograph for analysis. Product species were characterized by GC retention times when the product species obtained were commercially available and by GC–MS. Reference samples were used to produce standard curves for the quantitative analysis. The concentration of the products obtained in each case were determined with respect to the

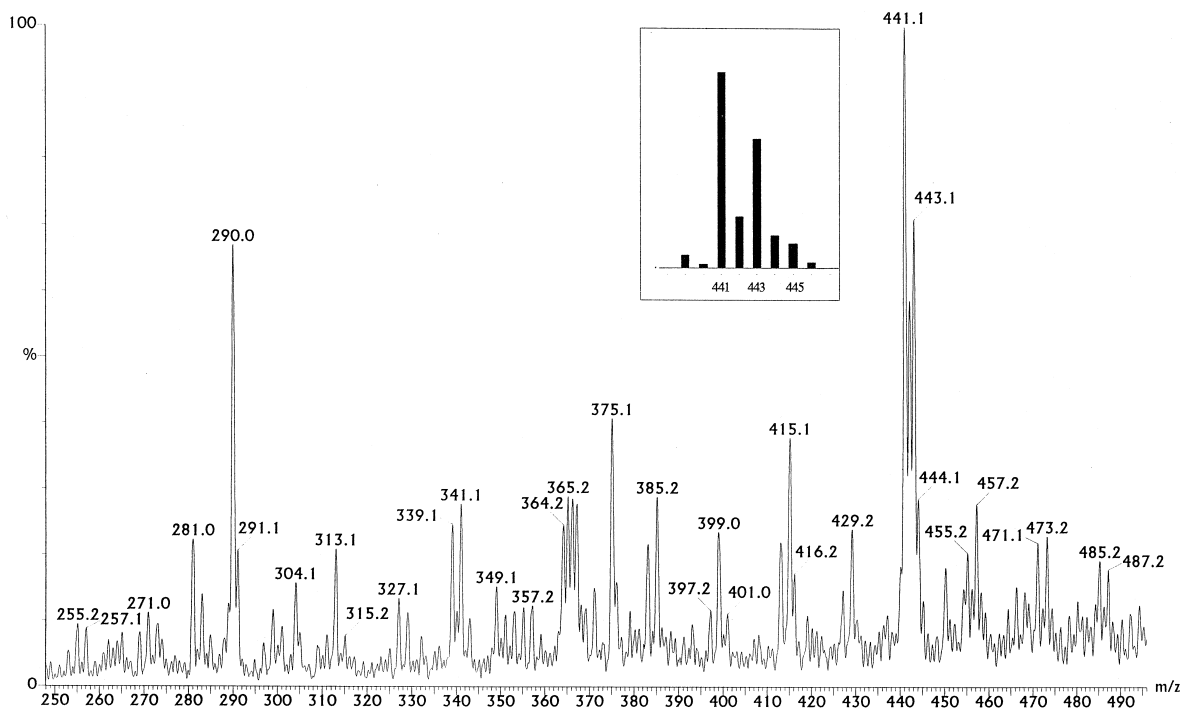


Fig. 1. Positive electrospray ionization mass spectra of FeCl<sub>2</sub>py<sub>4</sub><sup>+</sup>. The inset shows the calculated isotopic distribution.

biphenyl concentration (15 mM) that was always added to the reaction mixtures as an internal standard.

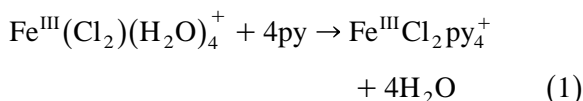
The experiments were designed to be limited by HOOH or *t*-BuOOH in order to evaluate reaction efficiency with respect to them and also to minimize secondary products.

### 3. Results

#### 3.1. Synthesis and characterization of the iron catalyst

A set of Fe and Co complexes has been tested in order to assess their capability to activate hydrogen peroxide for the catalytic transformation of aniline under mild conditions. Those compounds include,  $\text{Fe}^{\text{II}}(\text{bpy})_2^{2+}$ ,  $\text{Fe}^{\text{II}}(\text{CH}_3\text{CN})_4^{2+}$ ,  $\text{Fe}^{\text{II}}(\text{OPPh}_3)_4^{2+}$ ,  $\text{Fe}^{\text{II}}(\text{PA})_2$  (PA = 2-picolinate),  $\text{Fe}^{\text{III}}\text{Cl}_2\text{py}_4^+$  and  $\text{Co}^{\text{II}}(\text{bpy})_2^{2+}$ .  $\text{FeCl}_2\text{py}_4^+$  turned out to give the best results in terms of both product efficiencies and selectivities and the results obtained with this complex are reported below.

The iron catalyst  $\text{Fe}^{\text{III}}\text{Cl}_2\text{py}_4^+$  was prepared in situ by dissolving  $[\text{Fe}^{\text{III}}(\text{Cl}_2)(\text{H}_2\text{O})_4]\text{Cl} \cdot 2\text{H}_2\text{O}$  ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) [30] in pure pyridine,



The replacement of four water ligands from the original complex by four pyridine molecules is proved by electrospray ionization mass spectrometry (ESI-MS) spectroscopy. Fig. 1 shows the ESI-MS spectrum of a pyridine solution containing 5 mM  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ; a prominent ion cluster can be observed at  $m/z$  values corresponding to the molecular ion  $[\text{Fe}^{\text{III}}\text{Cl}_2\text{py}_4]^+$  ( $M-1$ )<sup>+</sup>. This assignment is further corroborated by the appearance of an isotope distribution pattern that is characteristic of the deduced formula (see the bar diagram in the inset of Fig. 1).

Cyclic voltammetric experiments were also carried out in order to further characterize the catalyst in pyridine solution and the voltammograms are exhibited in Fig. 2. Fig. 2A shows a cyclic voltammogram registered for  $\text{Fe}^{\text{III}}\text{Cl}_2\text{py}_4^+$  5 mM in a neat pyridine solution using  $(n\text{-Bu})_4\text{NPF}_6$  as the supporting electrolyte under inert atmosphere. The voltammogram shows the presence of a chemically reversible and electrochemically quasireversible redox process due to the  $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$  couple at  $E_{1/2} = 0.316$  V vs. SSCE ( $E_{\text{p,a}} = 0.432$  V,  $E_{\text{p,c}} = 0.200$  V). Fig. 2B shows the voltammogram obtained for a 1 M solution of aniline in pyridine. It can be clearly seen that no faradaic current flows for potentials between 0.0 and 0.4 V. At potentials higher

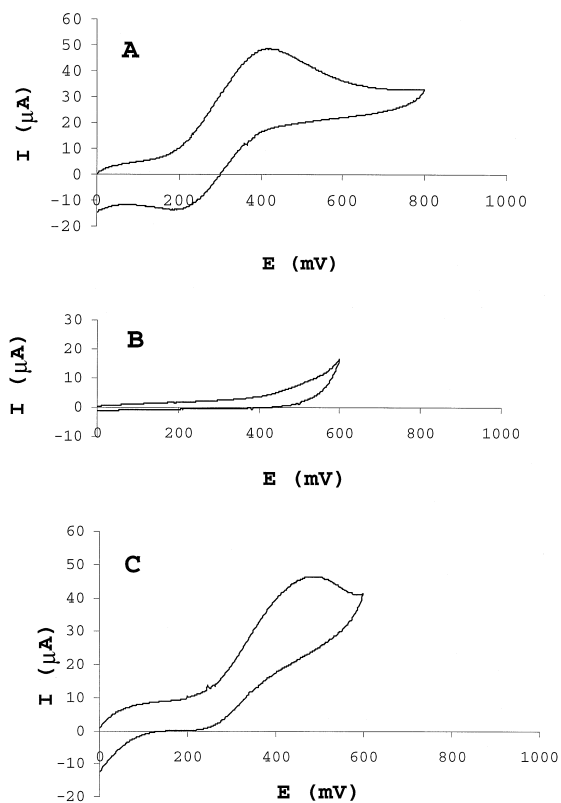


Fig. 2. Cyclic voltammetric experiments of: (A)  $\text{FeCl}_2\text{py}_4^+$  5 mM in pyridine; (B) aniline 1 M in pyridine; (C) a pyridine solution containing both  $\text{FeCl}_2\text{py}_4^+$  5 mM and aniline 1 M. For experimental details see Section 2.

than 0.4 V, an increase of the anodic current is observed which is due to the electrochemical oxidation of aniline. Fig. 2C shows the voltammogram obtained for a pyridine solution containing both 5 mM  $\text{Fe}^{\text{III}}\text{Cl}_2\text{py}_4^+$  and 1 M aniline. In this case, the anodic and cathodic peaks are shifted positively by 48 and 30 mV, respectively, with regard to the case with the metal catalyst alone together with a broadening of the anodic peak. This broadening is due to the simultaneous oxidation of Fe(II) to Fe(III) complex and the electrochemical oxidation of aniline. The peak shifting for the oxidation and reduction of the iron complex can be attributed to medium effects due to the presence of 1 M aniline.

ESI-MS and cyclic voltammetric experiments were also performed after running experiment 3 (Table 1) giving rise to a very similar spectrum and voltammogram, respectively, indicating that the iron catalyst,  $\text{Fe}^{\text{III}}\text{Cl}_2\text{py}_4^+$ , is fully recovered. This is further corroborated by the fact that upon adding more HOOH to the finished reaction the efficiency of the catalyst for the oxidation of aniline decreases only slightly with regard to the initial freshly prepared catalyst (see entries 3 and 19 of Table 1).

### 3.2. The transformation of aniline

The experiments presented in Table 1 deal with the transformation of aromatic amines by

Table 1  
 $\text{FeCl}_2\text{py}_4^+$  catalyzed transformation of aromatic anilines and its derivatives in pyridine

System conditions <sup>a</sup>					Products (mM $\pm$ 5%)				
Entry no.	<i>t</i> (min)	Cat <sup>b</sup> (mM)	Ox (mM)	Subs. (mM) <sub>2</sub> RPhNH <sub>2</sub>	RPhNO	RPhNO <sub>2</sub>	RPhNNPhR	RPhN(O) NPhR	Efficiency <sup>c</sup>
1	10	5	HOOH 100	R = H 1000	29.1	–	< 0.4	1.2	< 62.6
2	30	5	HOOH 100	R = H 1000	30.7	–	0.4	1.4	66.4
3	180	5	HOOH 100	R = H 1000	28.5	–	1.1	1.6	64.0
4	30	5	HOOH 100	R = Cl 1000	26.4	–	–	–	52.8
5	180	5	HOOH 100	R = Cl 1000	22.7	0.5	1.1	1.2	52.7
6	30	5	HOOH 100	R = Me 1000	35.8	–	–	–	71.6
7	180	5	HOOH 100	R = Me 1000	30.8	–	1.6	1.4	69.0
8	9840	5	HOOH 100	R = Me 1000	5.7	–	17.7	8.7	72.9
9	10	5	<i>t</i> -BuOOH 100	R = H 1000	–	7.5	–	–	22.5
10	10	5	HOOH 100 + PhNO 100	R = H 1000	123.8	2.3	0.7	5.1	71.2
11 <sup>d</sup>	10	5	PhNO 110	R = H 1000	110	–	0.5	0.7	3.1
12 <sup>d</sup>	10	5	PhNO 29	R = H 1000	29.0	–	0.1	0.2	0.8
13 <sup>d</sup>	180	5	PhNO 29	R = H 1000	28.0	–	1.0	0.8	4.4
14 <sup>d</sup>	180	–	PhNO 29	R = H 1000	29.0	–	0.1	0.2	0.8
15	180	5	HOOH 100	PhNNPh 2.5	–	–	2.5	–	0.0
16	180	5	HOOH 100 + PhNO 20	PhNNPh 2.5	6.1	7.3	2.4	0.1	
17	10	5	HOOH 400	R = H 1000	43.3	9.8	2.5	15.8	42.1
18	60	5	HOOH 400	R = H 1000	42.3	8.9	2.0	17.9	42.2
19	2 $\times$ 30	5	HOOH 2 $\times$ 100	R = H 1000	40.8	3.4	1.3	7.6	58.6
20	180	30	HOOH 100	R = H 1000	33.0	0.3	0.5	0.1	68.2
21	180	50	HOOH 100	R = H 1000	31.0	0.2	0.8	0.1	64.5
22 <sup>b</sup>	180	30	HOOH 100	R = H 1000	23.2	0.1	1.0	0.9	54.1
23 <sup>b</sup>	180	50	HOOH 100	R = H 1000	16.6	0.1	0.6	0.6	36.5

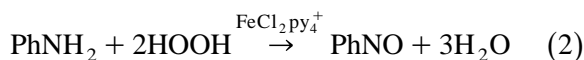
<sup>a</sup>Detailed system conditions are reported in Section 2.

<sup>b</sup> $\text{FeCl}_2\text{py}_4^+$  was used as catalyst for all the runs except for entries 22 and 23 which used  $\text{FeCl}_2\text{py}_4$ .

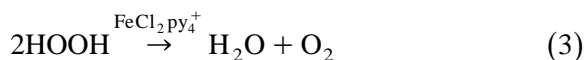
<sup>c</sup>Efficiencies are calculated with respect to HOOH. It is assumed that the formation of PhNO and PhNNPh from PhNH<sub>2</sub> require 2 molecules of HOOH whereas PhNO<sub>2</sub> and PhN(O)NPh require 3.

<sup>d</sup>Fifty-one microliters of H<sub>2</sub>O were added in order to reproduce initial reaction conditions.

HOOH when using  $\text{FeCl}_2\text{py}_4^+$  as the catalyst and pure pyridine as the solvent. Pure pyridine was used as the solvent because it gave higher efficiencies than pure acetonitrile, pure acetic acid and different combinations of them with pyridine. The  $\text{FeCl}_2\text{py}_4^+$  5 mM/HOOH 100 mM/ $\text{PhNH}_2$  1 M/pyridine system gave the best performance in terms of both selectivity and efficiency. After 10 min (see Table 1, entry 1) it yields mainly 29.1 mM PhNO with a small amount of other products and a reaction efficiency of 62.6% with regard to HOOH (representing more than 6 metal cycles and a turnover frequency of 0.61 cycles/min).

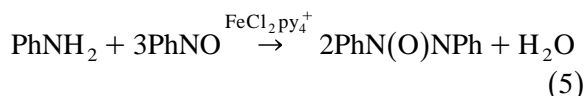
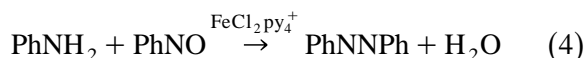


The remaining HOOH is transformed into water and dioxygen,



After 10 min reaction time, HOOH is completely depleted. If the reaction is allowed to proceed further till 3 h are elapsed (entry 3),

then GC analysis reveal the formation of significant amounts of azobenzene ( $\text{PhNNPh}$ ) and azoxybenzene ( $\text{PhN(O)NPh}$ ). The product distribution being: 28.5 mM PhNO, 1.1 mM PhN-NPh and 1.6 mM PhN(O)NPh; the overall efficiency is now 64.0%. The amount of the latter products increases with time whereas the opposite happens with the amount of nitrosobenzene in agreement with the following reactions,



A blank experiment shows that in the absence of either  $\text{FeCl}_2\text{py}_4^+$  or HOOH, under the present system conditions, aniline does not react at all. The same happens with aniline and nitrosobenzene; without  $\text{FeCl}_2\text{py}_4^+$  reactions (4) and (5) do not proceed at all (entry 14). For the reactions described above, the presence of air or 1 atm  $\text{O}_2$  does not significantly affect product distribution or kinetics.

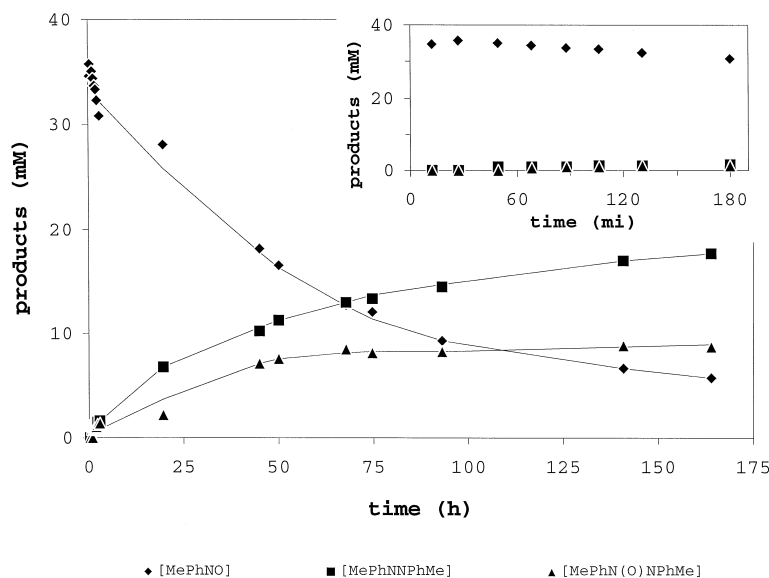


Fig. 3. Product profile vs. time for the system  $\text{FeCl}_2\text{py}_4^+$  5 mM/HOOH 100 mM/*p*-MePhNH<sub>2</sub> 1 M/pyridine. The inset shows the first 3 h of the reaction.

### 3.3. The transformation of phenyl-substituted anilines

The  $\text{FeCl}_2\text{py}_4^+$  catalyst can also be used to activate HOOH for the transformation of *para*-substituted anilines  $p\text{-RPhNH}_2$  ( $\text{R} = \text{Cl}, \text{H}, \text{Me}, \text{OMe}$ ). Table 1 shows the results obtained for the systems  $\text{FeCl}_2\text{py}_4^+$  5 mM/HOOH 100 mM/ $p\text{-RPhNH}_2$  1 M/pyridine after 30 min and 3 h reaction time (entries 2–8). As can be observed, toluidine ends up giving the higher yields whereas the Cl-substituted aniline gives the lowest manifesting an electrophilic character of the transition metal reactive species. A linear Hammett type of correlation between the initial rate constants and  $\sigma$  is obtained giving  $\rho = -0.3$ .

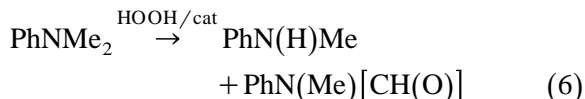
Fig. 3 shows the product profile vs. time for the system  $\text{FeCl}_2\text{py}_4^+$  5 mM/HOOH 100 mM/ $p\text{-MePhNH}_2$  1 M/pyridine. As can be observed from the graph, during the first 10 min of the reaction the only product significantly formed is the nitroso-derivative,  $p\text{-MePhNO}$  34.6 mM (nearly 7 metal cycles with a turnover frequency of 0.69 cycles/min) which is slowly converted into the corresponding azo- and azoxy-derivatives,  $p\text{-MePhNNPhMe-}p$  and  $p\text{-MePhN(O)NPhMe-}p$ . After 164 h (nearly 7 days, entry 8) reaction time the product distribution becomes  $p\text{-MePhNO}$  5.7 mM,  $p\text{-MePhN-NPhMe-}p$  17.7 mM and  $p\text{-MePhN(O)NPhMe-}p$  8.7 mM.

It is interesting to point out that *p*-anisidine is efficiently transformed, under the present system conditions, but it does not form any of the type of derivatives described in Table 1. In this case, a very insoluble polymeric material is obtained whose nature is under current investigation.

### 3.4. The transformation of *N*-substituted anilines

*N*-Substituted anilines were also reactive under the present system conditions:  $\text{FeCl}_2\text{py}_4^+$  5 mM/HOOH 100 mM/PhNRR' 1 M/pyridine. For  $\text{R} = \text{H}$ ;  $\text{R}' = \text{Me}$ , the reaction is not selec-

tive and a variety of different products is obtained (GC analysis indicates the presence of at least 12 different species). For  $\text{R} = \text{R}' = \text{Me}$ , the main product obtained is the monodemethylated amine,  $\text{PhN(H)Me}$  52.7 mM together with 13.8 mM  $\text{PhN(Me)[CH(O)]}$ ,



representing a reaction efficiency of over 80%.

## 4. Discussion

### 4.1. The formation of the nitroso-derivative and its fate

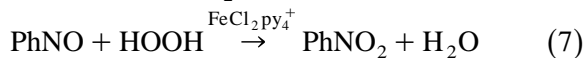
For aniline and phenyl substituted anilines, the results described in Table 1 for a 20:1 ratio Ox:Cat together with Fig. 3, indicate that at the early stages of the reaction the only product formed in a significant amount is the nitroso-derivative. Thus, HOOH is mainly being used to transform aniline into nitrosoaniline and once HOOH has disappeared, the azo- and azoxy-derivatives are formed at the expenses of  $\text{PhNO}$ . These processes are also catalyzed by  $\text{FeCl}_2\text{py}_4^+$  as shown by Eqs. (4) and (5) and evidenced by entry 14 of Table 1. Comparison of aza- and azoxy-derivatives product distribution in entries 1–3 with 12–13, indicate the presence of a potential alternative minor parallel pathway for the formation of  $\text{PhNNPh}$  and  $\text{PhN(O)NPh}$  at the very early stages of the reaction since higher amounts of them are produced in the former case.

From entries 15 and 16, it can also be inferred that neither HOOH nor  $\text{PhNO}$  in the presence of  $\text{FeCl}_2\text{py}_4^+$  are capable of transforming azobenzene into azoxybenzene.

### 4.2. The formation of nitro- and azoxy-derivatives

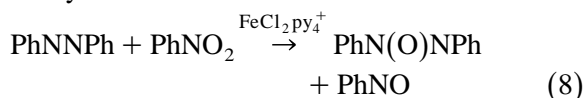
With an 80:1 ratio HOOH: $\text{FeCl}_2\text{py}_4^+$ , for instance the system  $\text{FeCl}_2\text{py}_4^+$  5 mM/HOOH

400 mM/PhNH<sub>2</sub> 1 M/pyridine (entries 17–18), an important amount of nitrobenzene, 9.8 mM, and azoxybenzene 15.8 mM are formed. These results suggest that in the presence of excess HOOH, FeCl<sub>2</sub>py<sub>4</sub><sup>+</sup> is capable of transforming PhNO into PhNO<sub>2</sub>,

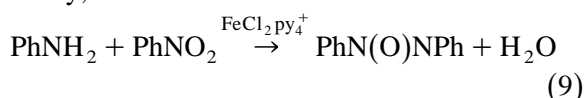


This is further corroborated by the experiments described in entries 10 and 16 where high amounts of the nitro-derivative are formed. Entry 16 clearly shows this point since azobenzene does not react with hydrogen peroxide (entry 15), therefore, nitrobenzene must be formed through Eq. (7).

The high amounts of azoxybenzene that are formed in entries 10 and 17 during the first 10 min of the reaction come necessarily from the interaction of nitrobenzene and azobenzene, since as stated above neither HOOH nor PhNO are capable of transforming azobenzene into azoxybenzene.

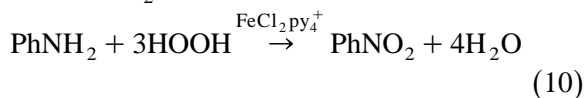


The formation of azoxy directly from aniline and nitrosobenzene, Eq. (5), is a minor parallel pathway in those particular cases. The direct interaction of aniline and nitrobenzene to form azoxy,



does not take place as shown by the experiment with *t*-BuOOH entry 9. The absence of azoxybenzene in entry 16 can be due to a very fast decomposition reaction of the catalyst with HOOH when aniline is not present.

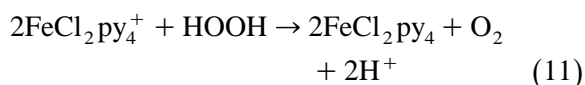
Replacement of HOOH by *t*-BuOOH dramatically changes the reaction products. The FeCl<sub>2</sub>py<sub>4</sub><sup>+</sup> 5 mM/*t*-BuOOH 100 mM/PhNH<sub>2</sub> 1 M/pyridine system (entry 9) yields only 7.5 mM PhNO<sub>2</sub>,



No other products are formed indicating the high selectivity of the system using *t*-BuOOH. In this particular case, the direct formation of nitrobenzene from aniline together with the absence of PhNO preclude the formation of both azo and azoxybenzene. Similar selectivity [2,25] has been described very recently in the literature when using *t*-BuOOH as the oxidant but with a chromium catalyst [2]. In this particular case, the presence of oxygen slightly increases the yield up to 8.4 mM PhNO<sub>2</sub> and keeps the selectivity unchanged.

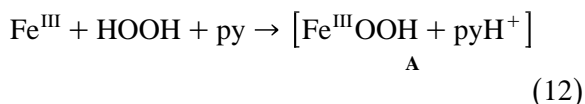
#### 4.3. The active species

The results described above clearly indicate that FeCl<sub>2</sub>py<sub>4</sub><sup>+</sup> is capable of activating HOOH for the transformation of aromatic amines. As pointed out very recently [33] the Fe(III) complex could initially be reduced by HOOH to form Fe(II),



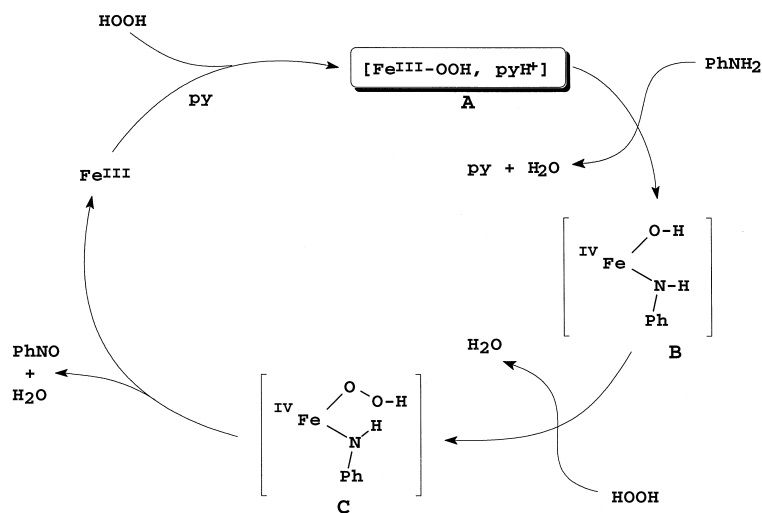
Entries 20–23 clearly indicate that within our particular working conditions this is not the case, since using initially FeCl<sub>2</sub>py<sub>4</sub> should significantly increase product yields specially with lower HOOH/Cat ratios and we observe just the opposite. The formation of a hypervalent iron-oxo (Fe<sup>V</sup> = O) intermediate seems unlikely given the electronegativity of the Cl ligands and their inability to stabilize a high-valent metal center [34]. Free hydroxyl radical HO· is also ruled out as active species since it yields mainly aromatic hydroxylations when it reacts with aniline [35], and those products have not been detected in any of our experiments.

Another possibility is nucleophilic addition/substitution of HOOH into FeCl<sub>2</sub>py<sub>4</sub><sup>+</sup> to form species **A** (see Scheme 1),



Early work by Halperin and Taube [36] had elegantly demonstrated the nucleophilic charac-





Scheme 1. Proposed reaction mechanism.

ter of HOOH towards Lewis bases. Evidence for the formation of reactive intermediates of type **A** have progressively and increasingly been obtained, with different instrumental techniques, when metal complexes react with peroxide and hydroperoxides, especially in organic solvents [25,33,37–45]. The reactive species **A** can abstract a hydrogen atom from aniline or from another molecule of hydrogen peroxide [33]. In Scheme 1, we propose a reaction mechanism where abstraction of hydrogen atom takes place from aniline since it is energetically favored by 2.6 kcal/mol [46] ( $\text{Ph(H)N-H}$ ,  $\Delta H_{\text{BDE}} = 86.4$  kcal/mol;  $\text{HOO-H}$ ,  $\Delta H_{\text{BDE}} = 89.0$  kcal/mol) and its concentration is one order of magnitude higher, forming intermediate **B** formally with bonded anilide and hydroxide ligands. Intermediate **B**, now interacts with a molecule of HOOH forming intermediate species **C**. Again the coordinated hydroperoxide can abstract a hydrogen atom in this case from the coordinated anilide ligand ejecting a water molecule with concomitant formation of  $\text{FeCl}_2\text{py}_4^+$  and nitrosobenzene. In the most favorable case, entry 17, more than 14 metal cycles are achieved with a turnover frequency of 1.4 cycles/min. PhNO is now the species from which all the rest of the products are formed as has been described in the present paper.

As a summary, the activation of HOOH and *t*-BuOOH by  $\text{FeCl}_2\text{py}_4^+$  allows the selective and effective transformation of aniline into its corresponding derivatives under very mild conditions. The oxygenated forms PhNO and  $\text{PhNO}_2$ , in turn, are also reactive species capable of using  $\text{FeCl}_2\text{py}_4^+$  to further transform aniline or its derivatives. Each reactive species has a characteristically differentiated reactivity. For instance, *t*-BuOOH is the only oxidative species capable of transforming aniline directly into nitrobenzene whereas the main product obtained with HOOH is the nitroso-derivative. Neither HOOH nor *t*-BuOOH are capable of directly transforming aniline into azobenzene. The interaction of PhNO and  $\text{PhNH}_2$  ends up forming azobenzene while aniline and nitrobenzene do not react. Finally, it is also interesting to mention that azobenzene is transformed into azoxybenzene with nitrobenzene but neither HOOH nor PhNO are capable of performing such reaction.

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## References

- [1] M.K. Stern, F.D. Hileman, J.K. Bashkin, *J. Am. Chem. Soc.* 114 (1992) 9247.
- [2] B. Jayachandran, M. Sasidharan, A. Sualai, T. Ravindranathan, *J. Chem. Soc., Chem. Commun.* (1995) 1523.
- [3] S. Forster, A. Rieker, K. Maruyama, K. Murata, A. Nishinaga, *J. Org. Chem.* 61 (1996) 3320.
- [4] M.D. Johnson, B.J. Hornstein, *J. Chem. Soc., Chem. Commun.* (1996) 965.
- [5] H. Firouzabadi, D. Mohajer, M. Entezari-Moghadam, *Bull. Chem. Soc. Jpn.* 61 (1988) 2185.
- [6] L. Delaude, P. Laszlo, P. Lehance, *Tetrahedron Lett.* 36 (1995) 8505.
- [7] S. Tollari, M. Cuscela, F. Porta, *J. Chem. Soc., Chem. Commun.* (1993) 1510.
- [8] S. Gontier, A. Tuel, *J. Catal.* 157 (1995) 124.
- [9] T. Selvam, A.V. Ramaswamy, *J. Chem. Soc., Chem. Commun.* (1996) 1215.
- [10] H.G. Zengel, *Chem.-Ing. Technol.* 55 (1983) 962.
- [11] G. Gowenlock, *Q. Rev. Chem. Soc.* 12 (1958) 321.
- [12] S. Sakaue, T. Tsubakino, Y. Nishiyama, Y. Ishii, *J. Org. Chem.* 58 (1993) 3633.
- [13] S. Tonti, P. Roffia, A. Cesana, M. Mantegazza, M. Padovan, *Eur. Pat.* 314 (1988) 147.
- [14] P.A. Adams, C. Adams, M.C. Berman, M.C. Lawrence, *J. Inorg. Biochem.* 20 (1984) 291.
- [15] J.J. Mieyal, J.L. Blumer, *J. Biol. Chem.* 251 (1976) 2442.
- [16] Y. Yasunaga, H. Nakanishi, N. Naka, T. Miki, T. Tsujimura, H. Itatani, A. Okuyama, K. Aozasa, *Lab. Invest.* 77 (1997) 677.
- [17] E. Pramauro, A.B. Prevot, V. Augugliaro, L. Palmisano, *Analyst* 120 (1995) 237.
- [18] P. Pillai, C.S. Helling, J. Dragun, *Chemosphere* 1 (1982) 299.
- [19] O.D. Wheeler, D. Gonzalez, *Tetrahedron* 20 (1964) 189.
- [20] R.R. Holmes, R.P. Bayer, *J. Am. Chem. Soc.* 82 (1960) 3454.
- [21] H.R. Gutman, *Experientia* 20 (1964) 128.
- [22] W.D. Emmons, *J. Am. Chem. Soc.* 79 (1957) 5528.
- [23] K.M. Ibne-Rasa, J.O. Edwards, *J. Am. Chem. Soc.* 84 (1962) 763.
- [24] Y. Ogata, H. Shimizu, *Bull. Chem. Soc. Jpn.* 52 (1979) 635.
- [25] G.R. Howe, R.R. Hiat, *J. Org. Chem.* 25 (1970) 4007.
- [26] K. Kosswig, *Justus Liebigs Ann. Chem.* 749 (1971) 206.
- [27] P. Burckard, J.P. Fleury, F. Weiss, *Bull. Soc. Chim. Fr.* (1965) 2730.
- [28] G. Barak, Y. Sasson, *J. Org. Chem.* 54 (1989) 3484.
- [29] K. Kinoshita, *Bull. Chem. Soc. Jpn.* 32 (1959) 780.
- [30] A.F. Wells, *Quimica Inorganica Estructural*, Reverte, Barcelona, 1978, pp. 24–25.
- [31] S. Carlino, M.J. Hudson, W.J. Locke, *J. Mater. Chem.* 7 (1997) 813.
- [32] J.P. Hage, A. Llobet, D.T. Sawyer, *Bioorg. Med. Chem.* 3 (1995) 1383.
- [33] D.T. Sawyer, A. Sobkowiak, T. Matsuhita, *Acc. Chem. Res.* 29 (1996) 409.
- [34] D.T. Sawyer, L. Spencer, H. Sugimoto, *Isr. J. Chem.* 28 (1987) 3.
- [35] G.V. Buxton, C.L. Greenstock, W.P. Helman, A.B. Ross, *J. Phys. Chem. Ref. Data* 17 (1988) 513.
- [36] J. Halperin, H. Taube, *J. Am. Chem. Soc.* 74 (1952) 380.
- [37] A. Sobkowiak, H.-C. Tung, D.T. Sawyer, *Prog. Inorg. Chem.* 40 (1992) 291.
- [38] D.T. Sawyer, C. Kang, A. Llobet, C. Redman, *J. Am. Chem. Soc.* 115 (1993) 5817.
- [39] D.H.R. Barton, B. Hu, D.K. Taylor, R.U.R. Wahl, *J. Chem. Soc., Perkin Trans. 2* (1996) 1031.
- [40] D.H.R. Barton, D.K. Taylor, *Pure Appl. Chem.* 68 (1996) 497.
- [41] M. Lubben, A. Meetsma, E.C. Wilkinson, B. Feringa, L. Que Jr., *Angew. Chem. Int. Ed. Engl.* 34 (1995) 1512.
- [42] S. Menage, E.C. Wilkinson, L. Que Jr., M. Fontecave, *M. Angew. Chem. Int. Ed. Engl.* 34 (1995) 203.
- [43] J. Kim, E. Larka, E.C. Wilkinson, L. Que Jr., *Angew. Chem. Int. Ed. Engl.* 34 (1995) 2048.
- [44] I. Yamazaki, L.H. Piette, *J. Am. Chem. Soc.* 113 (1991) 7588.
- [45] J. Kim, Y. Dong, E. Larka, L. Que Jr., *Inorg. Chem.* 35 (1996) 2369.
- [46] D.R. Lide (Ed.), *CRC Handbook of Chemistry and Physics*, 71st edn., CRC, Boca Raton, FL, 1990, pp. 9–85.