

# Iron(II, III)-catalyzed oxidative *N*-dealkylation of amines with dioxygen

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## Abstract

Labile iron complexes (e.g.,  $[\text{Fe}^{\text{III}}(\text{bpy})_2]_{\text{MeCN}}^{3+}$ ,  $[\text{Fe}^{\text{II}}(\text{bpy})_2]_{\text{MeCN}}^{2+}$ ,  $[\text{Fe}^{\text{III}}(\text{H}_2\text{O})_6]_{\text{MeCN}}^{3+}$ , and  $[\text{Fe}^{\text{II}}(\text{H}_2\text{O})_6]_{\text{MeCN}}^{2+}$ ) in base-free acetonitrile activate dioxygen for the direct oxygenation of *N,N*- and *N*-alkylated amines to form *N*-dealkylated products and corresponding aldehydes. *N,N*-dimethylaniline (DMA) is oxidized to *N*-methylaniline (MA) and formaldehyde as well as to *N*-methylanilide. Formaldehyde and the excess of substrate undergo condensation reaction to produce 4,4'-methylenebis(*N,N*-dimethylaniline) (MBDME). Small amounts of *N*-methylformanilide (MF) and formanilide are also formed during oxidation of *N,N*-dimethylaniline and *N*-methylaniline respectively. Iron(III) catalysts are reduced by the substrate to iron(II), which activates dioxygen. Dioxygen activation step is preceded by the equilibrium reaction between iron(II) catalyst and substrate.

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**Keywords:** *N*-demethylation; *N*-dealkylation; Dioxygen activation; Alkylated amines; Iron complexes

## 1. Introduction

Oxidations of amines are of considerable biological significance. Amines occur as amino acids, neurotransmitters and as components of the diet. Amine moieties are common in drugs and other xenobiotics ingested into the body [1]. *N*-dealkylation is a convenient method of degrading rich molecules, often with the result that they are transformed into more polar entities that are excreted from the body due to enhanced solubility. Moreover, an unprecedented mechanism of DNA alkylation damage repair by oxidative demethylation process has been recently described [2]. Therefore, the reaction attracts a lot of attention and several heme-proteins such as P-450 and peroxidases [3] and non-heme iron proteins [4] like lipoxigenases have been used as catalysts for the reaction. A number of model systems of *N*-dealkylation by means of chemical [3h,j,5] (including ligand dealkylation in a catalyst complex [5t–z]), electrochemical [6], and photochemical [7] methods have also been studied. These model reactions are often performed with various alternative oxygen sources including iodosobenzene and hydroperoxides in the presence of appropriate iron or other metal complexes. Except for ligand

dealkylation processes, dioxygen as a direct oxidant has been little studied [5b,j,k,n].

In spite of the large number of studies important uncertainties over the mechanism of oxidative *N*-dealkylation by cytochrome P450 still persist [8]. One mechanism suggests that *N*-dealkylation involves a classical hydrogen atom transfer (HAT) - hydroxyl recombination sequence. The other one assumes that the *N*-dealkylation process is initiated by abstracting an electron from the amine (single electron transfer (SET)). Recent reports [3z,9] postulate the direct oxygen atom transfer from metal-dioxygen adduct to organic molecule in the concerted C–H insertion mechanism. It includes the involvement of dioxygen adducts either (peroxo)diiron(III) or di(oxo)diiron(IV) as reactive intermediates that first hydroxylate the C–H bonds  $\alpha$  to the nitrogen affording the *N*-demethylated product and corresponding aldehyde or ketone as a final product.

In our previous studies [5k] we have found that in acetonitrile  $[\text{Co}^{\text{II}}(\text{bpy})_2](\text{ClO}_4)_2$  activates dioxygen via the reversible formation of a  $\mu$ -dioxygen complex. The complex dehydrogenates (oxidizes) *N*-methylanilines to give formaldehyde and the demethylated aniline. The reaction is first-order with respect to the concentrations of catalyst, dioxygen, and substrate. When hydrogen peroxide is used as the oxidant, *N*-methylamides are also present among the products. The  $[\text{Co}^{\text{II}}(\text{bpy})_2]^{2+}/\text{O}_2$  complex does not react however, with hydrocarbons. Even 1,4-cyclohexadiene

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(C–H bond energy,  $\Delta H_{\text{DBE}} = 73 \text{ kcal mol}^{-1}$ ) remains unchanged in the reaction mixture after 72 h. The absence of any activation by  $[\text{Co}^{\text{II}}(\text{bpy})_2]^{2+}$  for oxidation of 1,4-cyclohexadiene by dioxygen indicates that the reactive species formed in the system are unable to abstract even weakly bounded hydrogen atoms. In contrast, the oxidation of *N*-methylanilines ( $\Delta H_{\text{DBE}}$  for the C–H and N–H bonds is about 90–95  $\text{kcal mol}^{-1}$ ) appears to occur by the removal of two hydrogen atoms in a single step. The first-order dependence of the reaction rate with respect to the catalyst, dioxygen, and substrate concentrations is consistent with substrate binding to  $[\text{Co}^{\text{II}}(\text{bpy})_2]^{2+}$  in an initial reversible step, which is followed by the formation of the  $\mu$ -dioxygen reaction complex. The later facilitates the almost concerted removal of two hydrogen atoms from each bound substrate to form demethylated aniline, formaldehyde and water molecules. The lack of reactivity for aniline and *N*-phenylaniline is consistent with this proposition. The presence of secondary product - 4,4'-methylenebis(*N,N*-dimethylaniline) (MBDMA) - formed in the consecutive reaction between *N,N*-dimethylaniline and formaldehyde confirms the suggested dehydrogenation pathway.

Our recent studies have indicated that redox properties of iron catalyst have crucial role in the oxidation of hydrocarbons by dioxygen and hydrogen peroxide. Labile iron(III) complexes in base-free acetonitrile are reduced by cyclohexene even in the presence of dioxygen [10], and also by hydrogen peroxide [11]. Therefore, we have undertaken the investigations on oxidation of *N,N*-dimethylaniline and other alkylated anilines by dioxygen, air, and hydrogen peroxide catalyzed by several labile iron complexes ( $[\text{Fe}^{\text{III}}(\text{bpy})_2]_{\text{MeCN}}^{3+}$ ,  $[\text{Fe}^{\text{II}}(\text{bpy})_2]_{\text{MeCN}}^{2+}$ ,  $[\text{Fe}^{\text{III}}(\text{H}_2\text{O})_6]_{\text{MeCN}}^{3+}$ ,  $[\text{Fe}^{\text{II}}(\text{H}_2\text{O})_6]_{\text{MeCN}}^{2+}$ ) in acetonitrile.

## 2. Experimental

### 2.1. Equipment

The reaction products were separated and identified with a Hewlett–Packard 4890A Series gas chromatograph (GC) equipped with an HP-1 capillary column (cross-linked methyl-silicone-gum phase, 12 m  $\times$  0.2 mm i.d.) and by gas chromatography–mass spectrometry (MS) (Agilent Technologies 6890N gas chromatograph with 5973N mass-selective detector). A three-electrode potentiostat (Bioanalytical Systems Model CV-50W) was used to record the cyclic voltammograms (CV). The experiments were conducted in a 15 mL electrochemical cell with provision to control the presence of dioxygen with an argon-purge system. The working electrode was a Bioanalytical Systems glassy-carbon inlay (area, 0.09  $\text{cm}^2$ ), the auxiliary electrode a platinum wire (contained in a glass tube with a medium porosity glass-frit and filled with a solution of supporting electrolyte), and the reference electrode a Ag/AgCl wire

in an aqueous tetramethylammonium chloride solution that was adjusted to give a potential of 0.00 V versus SCE. The latter was contained in a Pyrex tube with a cracked soft-glass tip, which was placed inside a Luggin capillary [12]. The UV-vis spectrophotometric measurements were made with a Hewlett-Packard Model HP-8453 diode array rapid scan spectrophotometer.

### 2.2. Chemicals and reagents

The reagents for the investigations and syntheses were the highest purity commercially available and were used without further purification. The solvent for all of the experiments was Burdick and Jackson “distilled in glass” grade acetonitrile (MeCN, 0.002%  $\text{H}_2\text{O}$ ). High-purity argon gas was used to deaerate the solutions. Tetraethylammonium perchlorate (TEAP, GFS Chemicals) was dried in vacuo over  $\text{CaSO}_4$  for 24 h prior to use. Iron(II) and (III) perchlorates,  $\text{Fe}^{\text{II}}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (99+%) and  $\text{Fe}^{\text{III}}(\text{ClO}_4)_3 \cdot 9\text{H}_2\text{O}$  (99+%) were obtained from GFS Chemicals. The organic substances included: 2,2'-bipyridine (bpy, 99+%), aniline [ $\text{C}_6\text{H}_5\text{NH}_2$ , 99.5+ %], *N,N*-dimethylaniline [DMA,  $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$ , 99.5+ %], *N*-methylaniline [MA,  $\text{C}_6\text{H}_5\text{NH}(\text{CH}_3)$ , 99+ %], *N,N*-diethylaniline [DEA,  $\text{C}_6\text{H}_5\text{N}(\text{C}_2\text{H}_5)_2$ , 99+ %], *N*-ethylaniline [EA,  $\text{C}_6\text{H}_5\text{NH}(\text{C}_2\text{H}_5)$ , 98%], *N*-methylformanilide [MF,  $\text{HCON}(\text{CH}_3)\text{C}_6\text{H}_5$ , 99%], formanilide [ $\text{HCONHC}_6\text{H}_5$ , 99%], 4,4'-methylenebis(*N,N*-dimethylaniline) ( $\text{CH}_2[\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2]_2$  98%), biphenyl (PhPh, 99+%), and diphenyl diselenide [ $\text{PhSeSePh}$  98%] were obtained from Aldrich.

*Synthesis of  $[\text{Fe}^{\text{II}}(\text{MeCN})_4](\text{ClO}_4)_2$* : The  $[\text{Fe}^{\text{II}}(\text{MeCN})_4](\text{ClO}_4)_2$  complex was prepared by multiple recrystallizations of  $[\text{Fe}^{\text{II}}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$  from MeCN [13,14].

*Iron(II) bis(2,2'-bipyridine)*: The  $[\text{Fe}^{\text{II}}(\text{bpy})_2]_{\text{MeCN}}^{2+}$  complex was prepared in-situ by mixing  $[\text{Fe}^{\text{II}}(\text{MeCN})_4](\text{ClO}_4)_2$  in MeCN with a stoichiometric ratio of bipyridine. The other metal complexes were prepared in situ by mixing the corresponding salt with stoichiometric ratios of ligand in acetonitrile.

### 2.3. Methods

The appropriate amounts of metal salt and ligand were combined in acetonitrile followed by the addition of substrate (1 M) (total volume = 5 ml). The solution was saturated with dioxygen ( $\text{O}_2$ , 1 atm) or air ( $\text{O}_2$ , 0.2 atm) or high-purity argon gas ( $\text{O}_2$ , 0 atm). The reaction cell (25  $\text{cm}^3$  vial with cut-out cap and Teflon-faced septum) had a 20-ml headspace, which provided a reservoir to maintain a constant solution concentration of dioxygen. The reactions were allowed to proceed for 24 h with constant stirring at room temperature ( $23 \pm 1$  °C). After the experiment samples of the reaction solution were injected into a capillary-column gas chromatograph for analysis. In some cases the reaction was quenched with water, and the product solution was extracted with diethyl ether. Product species were characterized by

GC–MS. Authentic samples were always used to confirm product identifications and to produce standard curves for quantitative assays of the product species. Biphenyl (10 mM) was used as an internal standard. All experiments were done in triplicate. The presented values of concentration are the mean values of three independent experiments.

### 3. Results

In acetonitrile simple iron(II) and iron(III) complexes activate dioxygen to oxygenate *N,N*-dimethylaniline to yield *N*-methylaniline (MA), *N*-methylformanilide (MF), and 4,4'-methylenebis(*N,N*-dimethylaniline) (MBDMA) (Table 1). Under argon atmosphere only traces of products were detected. The product profiles after 24 h reaction time indicate that the 1 mM  $[\text{Fe}^{\text{II}}(\text{bpy})_2]_{\text{MeCN}}^{2+}/\text{O}_2$  (1 atm) combination is the most reactive - 48.8 products/catalyst turnovers; with air (0.21 atm  $\text{O}_2$ ), however the reaction rate is reduced only to 34.1 product/catalyst turnovers. [To calculate product/catalyst turnover, the amounts of 4,4'-methylenebis(*N,N*-dimethylaniline), as a product of consecutive reaction between *N,N*-dimethylaniline and formaldehyde, was not taken into account]. The use of Fe(III) instead of Fe(II) causes the reaction yield slightly to decrease. Fig. 1A and B show typical dependences of products concentrations versus time for  $[\text{Fe}^{\text{II}}(\text{H}_2\text{O})_6]_{\text{MeCN}}^{2+}$  and  $[\text{Fe}^{\text{II}}(\text{bpy})_2]_{\text{MeCN}}^{2+}$  as catalysts, respectively. The presented plot indicates that the reaction is completed after approx-

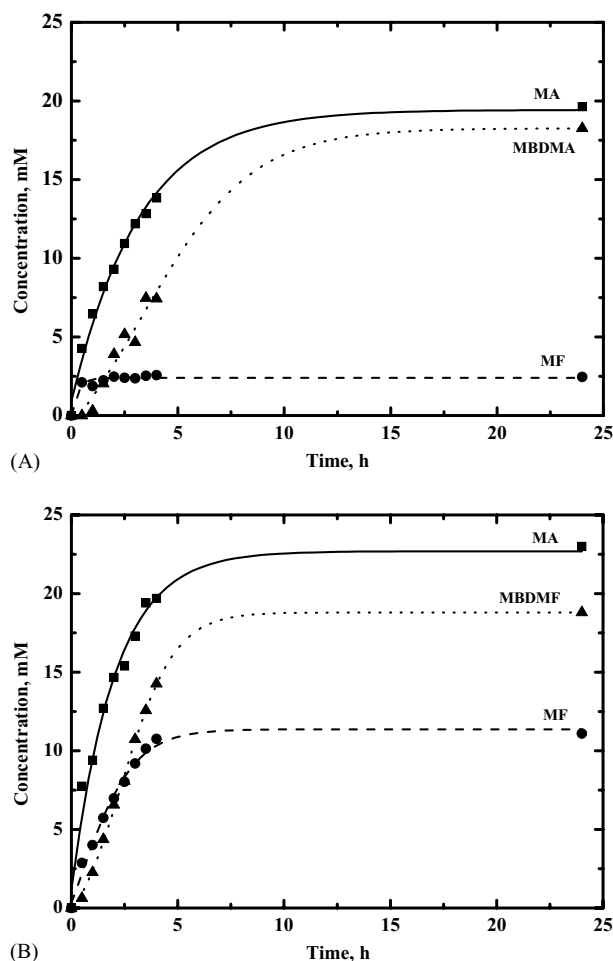


Fig. 1. Dependence of products concentration on time for oxidation of 1 M *N,N*-dimethylaniline in acetonitrile by air catalyzed by: (A) 1 mM  $[\text{Fe}^{\text{II}}(\text{H}_2\text{O})_6]_{\text{MeCN}}^{2+}$  and (B) 1 mM  $[\text{Fe}^{\text{II}}(\text{bpy})_2]_{\text{MeCN}}^{2+}$ .

Table 1

Iron-induced oxidation of 1 M *N,N*-dimethylaniline by dioxygen and air to produce *N*-methylaniline, *N*-methylformanilide, and 4,4'-methylenebis(*N,N*-dimethylaniline)

Catalyst	Oxidant	MA (mM)	MF (mM)	MBDMA (mM)
1 mM $[\text{Fe}^{\text{II}}(\text{H}_2\text{O})_6]_{\text{MeCN}}^{2+}$	$\text{O}_2$	21.9	2.3	18.0
1 mM $[\text{Fe}^{\text{II}}(\text{H}_2\text{O})_6]_{\text{MeCN}}^{2+}$	Air	19.6	2.5	18.3
1 mM $[\text{Fe}^{\text{III}}(\text{H}_2\text{O})_6]_{\text{MeCN}}^{3+}$	$\text{O}_2$	22.9	2.4	18.7
1 mM $[\text{Fe}^{\text{III}}(\text{H}_2\text{O})_6]_{\text{MeCN}}^{3+}$	Air	15.6	2.0	13.3
1 mM $[\text{Fe}^{\text{II}}(\text{bpy})_2]_{\text{MeCN}}^{2+}$	$\text{O}_2$	31.4	17.4	22.1
1 mM $[\text{Fe}^{\text{II}}(\text{bpy})_2]_{\text{MeCN}}^{2+}$	$\text{O}_2$ , $\text{Ph}_2\text{Se}_2^{\text{a}}$	5.8	12.6	7.8
1 mM $[\text{Fe}^{\text{II}}(\text{bpy})_2]_{\text{MeCN}}^{2+}$	Air	23.0	11.1	19.3
1 mM $[\text{Fe}^{\text{III}}(\text{bpy})_2]_{\text{MeCN}}^{3+}$	$\text{O}_2$	23.3	5.3	16.6
1 mM $[\text{Fe}^{\text{III}}(\text{bpy})_2]_{\text{MeCN}}^{3+}$	Air	14.8	2.1	12.3
16 mM $[\text{Fe}^{\text{II}}(\text{H}_2\text{O})_6]_{\text{MeCN}}^{2+}$	$\text{O}_2$	30.6	2.7	22.1
16 mM $[\text{Fe}^{\text{II}}(\text{H}_2\text{O})_6]_{\text{MeCN}}^{2+}$	Air	22.8	2.4	5.7
16 mM $[\text{Fe}^{\text{III}}(\text{H}_2\text{O})_6]_{\text{MeCN}}^{3+}$	$\text{O}_2$	37.1	3.2	10.8
16 mM $[\text{Fe}^{\text{II}}(\text{bpy})_2]_{\text{MeCN}}^{2+}$	$\text{O}_2$	38.4	3.6	29.4
16 mM $[\text{Fe}^{\text{II}}(\text{bpy})_2]_{\text{MeCN}}^{2+}$	Air	21.7	3.9	9.2
16 mM $[\text{Fe}^{\text{III}}(\text{bpy})_2]_{\text{MeCN}}^{3+}$	$\text{O}_2$	32.1	3.8	16.4

Reaction time: 24 h.

<sup>a</sup> Concentration of  $\text{PhSeSePh}$  equal to 0.1 M, no coupling products -SePh were detected.

imately 10 h, the concentration profiles of *N*-methylaniline and 4,4'-methylenebis(*N,N*-dimethylaniline) are similar, and the final concentration of the later is slightly smaller. The concentration of *N*-methylformanilide is generally smaller than the other products. The presence of a radical trap diphenyl diselenide ( $\text{PhSeSePh}$ , 0.1 M) in the reaction system causes the decrease of the reaction yield, however no coupling products with -SePh were detected.

The values of initial reaction rates indicate that: (a) the use of 1 mM  $[\text{Fe}^{\text{II}}(\text{bpy})_2]_{\text{MeCN}}^{2+}$  instead of 1 mM  $[\text{Fe}^{\text{II}}(\text{H}_2\text{O})_6]_{\text{MeCN}}^{2+}$  as catalyst causes the initial reaction rate to increase (15.0 versus 9.2 and 12.3 versus 8.6 for dioxygen and air, respectively), the effect is not so visible when the concentration of the catalyst is equal to 16 mM; (b) the use of air instead dioxygen causes only slight decrease in the initial reaction rates. The last observation is also supported by the results presented in Table 1. The decrease of dioxygen concentration 4.8 times by the use of air (1/0.21) causes the decrease of the amounts of products after 24 h approximately 1.5 times, which also indicates that the reaction order with respect to dioxygen is less than 1.

Table 2

Iron-induced oxidation of 1 M *N*-methylaniline and *N*-ethylaniline by dioxygen and air to produce aniline

Catalyst	Oxidant	Aniline from <i>N</i> -methylaniline mM	Aniline from <i>N</i> -ethylaniline mM
1 mM [Fe <sup>II</sup> (H <sub>2</sub> O) <sub>6</sub> ] <sub>MeCN</sub> <sup>2+</sup>	O <sub>2</sub>	5.6	3.5
1 mM [Fe <sup>II</sup> (H <sub>2</sub> O) <sub>6</sub> ] <sub>MeCN</sub> <sup>2+</sup>	Air	7.4	3.6
1 mM [Fe <sup>III</sup> (H <sub>2</sub> O) <sub>6</sub> ] <sub>MeCN</sub> <sup>3+</sup>	O <sub>2</sub>	1.4	1.7
1 mM [Fe <sup>II</sup> (bpy) <sub>2</sub> ] <sub>MeCN</sub> <sup>2+</sup>	O <sub>2</sub>	8.2	6.5
1 mM [Fe <sup>II</sup> (bpy) <sub>2</sub> ] <sub>MeCN</sub> <sup>2+</sup>	Air	11.0	3.6
1 mM [Fe <sup>III</sup> (bpy) <sub>2</sub> ] <sub>MeCN</sub> <sup>3+</sup>	O <sub>2</sub>	13.5	6.9
16 mM [Fe <sup>II</sup> (H <sub>2</sub> O) <sub>6</sub> ] <sub>MeCN</sub> <sup>2+</sup>	O <sub>2</sub>	15.2	6.4
16 mM [Fe <sup>II</sup> (H <sub>2</sub> O) <sub>6</sub> ] <sub>MeCN</sub> <sup>2+</sup>	Air	12.1	6.3
16 mM [Fe <sup>III</sup> (H <sub>2</sub> O) <sub>6</sub> ] <sub>MeCN</sub> <sup>3+</sup>	O <sub>2</sub>	8.8	8.1
16 mM [Fe <sup>II</sup> (bpy) <sub>2</sub> ] <sub>MeCN</sub> <sup>2+</sup>	O <sub>2</sub>	11.5	4.7
16 mM [Fe <sup>II</sup> (bpy) <sub>2</sub> ] <sub>MeCN</sub> <sup>2+</sup>	Air	12.0	8.1
16 mM [Fe <sup>III</sup> (bpy) <sub>2</sub> ] <sub>MeCN</sub> <sup>3+</sup>	O <sub>2</sub>	3.5	5.9

Reaction time: 24 h.

The described iron catalyst/dioxygen systems convert also *N*-methylaniline to aniline and traces of formanilide, as well as *N*-ethylaniline to aniline. The yields of these reactions however, are much smaller than in the case of *N,N*-dimethylaniline (Table 2). When *N,N*-diethylaniline was used as a substrate, only traces of aniline were detected after 24 h reaction time.

Generally, in all reactions (Tables 1 and 2) the presence of 2,2'-bipyridine as a ligand causes an increase in the products yield, Fe(III) is a less effective catalyst than Fe(II), the decrease of catalyst concentration increases the product/catalyst turnover ratio, and the reaction order with respect to dioxygen is <1.

Fig. 2 illustrates the oxidation/reduction character of the catalyst/substrate system. Cyclic-voltammetric measurements indicate that the 2:1 (molar ratio) combination of [Fe<sup>III</sup>(H<sub>2</sub>O)<sub>6</sub>]<sub>MeCN</sub><sup>3+</sup> with *N,N*-dimethylaniline causes the appearance of Fe(II) oxidation peak—curve 3 in Fig. 2a (for the clarity only the anodic scans of the cyclic voltammograms were shown). The peak, however, is shifted towards more negative potentials (from +1.6 to +1.4 V) in comparison to the Fe(II) oxidation peak in the absence of DMA, which is presented by curve 4. At the same time the disappearance of the substrate (DMA) oxidation peak (curve 2) is observed. Similar effects exist when [Fe<sup>III</sup>(bpy)<sub>2</sub>]<sub>MeCN</sub><sup>3+</sup> is used in place of [Fe<sup>III</sup>(H<sub>2</sub>O)<sub>6</sub>]<sub>MeCN</sub><sup>3+</sup> (Fig. 2b). The cyclic voltammogram of the acetonitrile solution of 1:2 combination of Fe(II) and bpy (curve 4) shows three oxidation peaks, which can be attributed to: [Fe<sup>II</sup>(bpy)<sub>3</sub>]<sub>MeCN</sub><sup>2+</sup> (+1.15 V) [15], [Fe<sup>II</sup>(bpy)<sub>2</sub>]<sub>MeCN</sub><sup>2+</sup> (+1.35 V), and [Fe<sup>II</sup>(H<sub>2</sub>O)<sub>6</sub>]<sub>MeCN</sub><sup>2+</sup> (+1.6 V) whereas the combination of Fe(III) with bpy does not show any anodic peaks (curve 1). The addition of DMA to the solution of [Fe<sup>III</sup>(bpy)<sub>2</sub>]<sub>MeCN</sub><sup>3+</sup> causes the appearance of Fe(II) oxidations peaks (curve 3 - the second and third

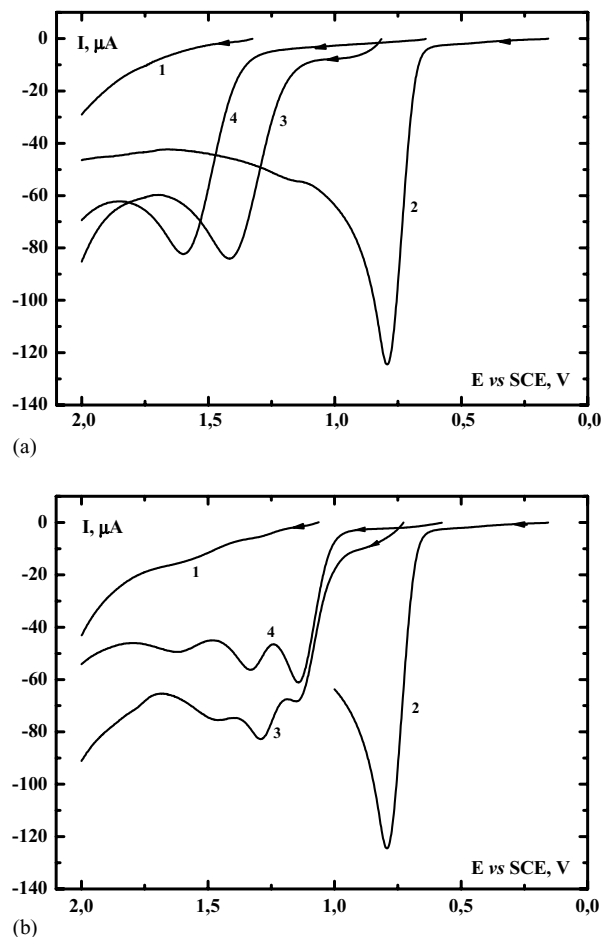


Fig. 2. Voltammograms in acetonitrile of: (a) (1) 5 mM [Fe<sup>III</sup>(H<sub>2</sub>O)<sub>6</sub>]<sub>MeCN</sub><sup>3+</sup>; (2) 2.5 mM *N,N*-dimethylaniline, (3) combination of 5 mM [Fe<sup>III</sup>(H<sub>2</sub>O)<sub>6</sub>]<sub>MeCN</sub><sup>3+</sup> and 2.5 mM *N,N*-dimethylaniline after 2 h in argon atmosphere, and (4) 5 mM [Fe<sup>II</sup>(H<sub>2</sub>O)<sub>6</sub>]<sub>MeCN</sub><sup>2+</sup>; (b) 5 mM [Fe<sup>III</sup>(bpy)<sub>2</sub>]<sub>MeCN</sub><sup>3+</sup>; (2) 2.5 mM *N,N*-dimethylaniline, (3) combination of 5 mM [Fe<sup>III</sup>(bpy)<sub>2</sub>]<sub>MeCN</sub><sup>3+</sup> and 2.5 mM *N,N*-dimethylaniline after 2 h in argon atmosphere, and (4) 5 mM [Fe<sup>II</sup>(bpy)<sub>2</sub>]<sub>MeCN</sub><sup>2+</sup>.

peaks however, are shifted towards more negative potentials) and the disappearance of DMA oxidation peak. The complete disappearance of substrate occurs in the range of Fe(III) to DMA molar ratios from 2:1 to 1:2. Analogous behavior was observed when other substrates were used. The results presented in Fig. 2 indicate that Fe(III) is reduced to Fe(II) by methylated anilines and that there are interactions between Fe(II) and methylated anilines or products of their oxidation.

To confirm the last statement the cyclic-voltammetry of Fe(II)/DMA system was performed. After mixing the reagents the oxidation peak of DMA is lowered (Fig. 3a, curve 1) and oxidation peak of [Fe<sup>II</sup>(H<sub>2</sub>O)<sub>6</sub>]<sub>MeCN</sub><sup>2+</sup> is slightly shifted towards more positive potentials (Fig. 3a, curve 2). After 2 h under Ar atmosphere the DMA oxidation peak almost completely disappeared and Fe(II) oxidation peak is moved towards more negative potentials (Fig. 3a, curve 3) as observed during interaction between Fe(III) and DMA.

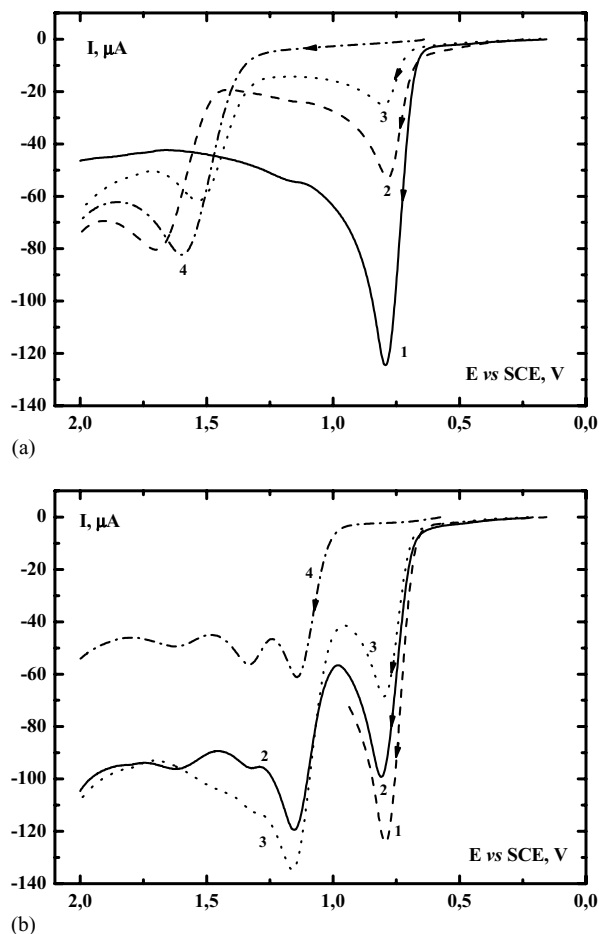


Fig. 3. Voltammograms in acetonitrile of: (a) (1) 2.5 mM *N,N*-dimethylaniline, (2) combination 5 mM  $[\text{Fe}^{\text{II}}(\text{H}_2\text{O})_6]_{\text{MeCN}}^{2+}$  and 2.5 mM *N,N*-dimethylaniline after mixing, (3) the same as (2) after 2 h in argon atmosphere, and (4) 5 mM  $[\text{Fe}^{\text{II}}(\text{H}_2\text{O})_6]_{\text{MeCN}}^{2+}$ ; (b) (1) 2.5 mM *N,N*-dimethylaniline, (2) combination 5 mM  $[\text{Fe}^{\text{II}}(\text{bpy})_2]_{\text{MeCN}}^{2+}$  and 2.5 mM *N,N*-dimethylaniline after mixing, (3) the same as (2) after 2 h in argon atmosphere, and (4) 5 mM  $[\text{Fe}^{\text{II}}(\text{bpy})_2]_{\text{MeCN}}^{2+}$ .

Again, in Fig. 3 only anodic scans were shown for clarity. When labile Fe(II)-bpy complex is used the existence of interactions between Fe(II) and DMA is not so clearly visible. However, the decrease of the height of DMA oxidation peak in time is observed and the height of the peak corresponding to coordinately saturated Fe(II) complex (at +1.15 V, by analogy to  $[\text{Fe}^{\text{II}}(\text{bpy})_3]_{\text{MeCN}}^{2+}$ ) is increased (Fig. 3b, curve 3). As previously, the analogous situation occurs in the range of Fe(II) to DMA molar ratios from 2:1 to 1:2, and similar effects were observed when other methylated anilines were used instead of DMA. These results also indicate that interactions between Fe(II) and methylated amines occur.

The interactions between  $[\text{Fe}^{\text{III}}(\text{H}_2\text{O})_6]_{\text{MeCN}}^{3+}$  and DMA were also investigated spectrometrically. When the compounds are combined in acetonitrile in argon atmosphere the absorption band of DMA disappears and a new band appears at  $\lambda_{\text{max}} = 465 \text{ nm}$  (Fig. 4). This behavior was observed from 2:1 up to 1:3 Fe(III)/DMA molar ratios. If however, the one mole equivalent of  $\text{H}^+$  was added to DMA

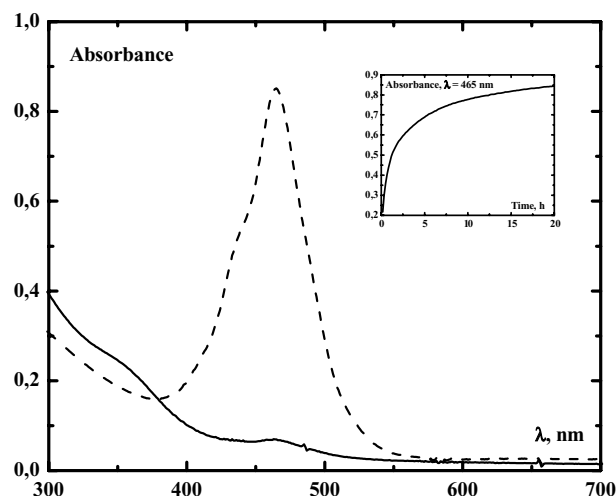


Fig. 4. The UV-Vis spectrum for the combination of 0.1 mM *N,N*-dimethylaniline and 0.1 mM  $[\text{Fe}^{\text{III}}(\text{H}_2\text{O})_6]_{\text{MeCN}}^{3+}$  in acetonitrile in argon atmosphere. Inset: the dependence of absorbance at  $\lambda = 465 \text{ nm}$  on time.

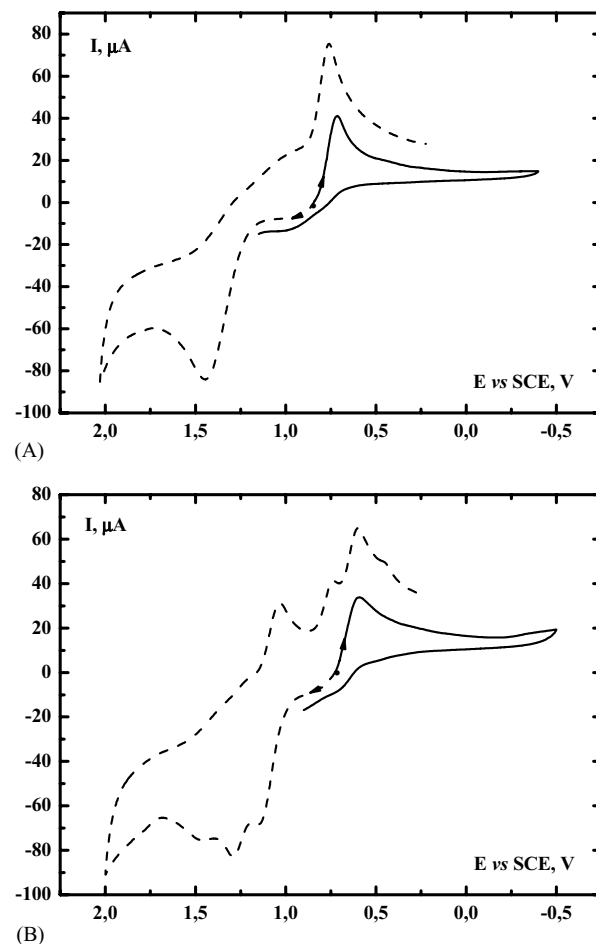
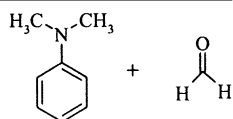


Fig. 5. Voltammograms in acetonitrile of: (A) combination of 5 mM  $[\text{Fe}^{\text{III}}(\text{H}_2\text{O})_6]_{\text{MeCN}}^{3+}$  and 2.5 mM *N,N*-dimethylaniline; (B) combination of 5 mM  $[\text{Fe}^{\text{III}}(\text{bpy})_2]_{\text{MeCN}}^{3+}$  and 2.5 mM *N,N*-dimethylaniline; both after 2 h in argon atmosphere.



the effect occurred also for higher Fe(III)/DMA ratios. The height of the band increases initially and then either reaches a plateau (for 2:1 Fe(III)/DMA molar ratios, Fig. 4, inset) or decreases (for higher Fe(III)/DMA ratios). When Fe(II) catalyst is used instead of Fe(III) there are no new peaks present on the UV spectra. The described effect is less visible (lower absorption peak height) in the presence of dioxygen in the solution. The replacement of  $[\text{Fe}^{\text{III}}(\text{H}_2\text{O})_6]_{\text{MeCN}}^{3+}$  by Fe(III)-bpy complex also attenuates the observed effect. In addition, the described absorption band slightly overlaps with  $[\text{Fe}^{\text{II}}(\text{bpy})_3]_{\text{MeCN}}^{2+}$  adsorption peak, which presence indicates that Fe(II) is formed in the reaction. When the described UV-Vis absorption band is present, on



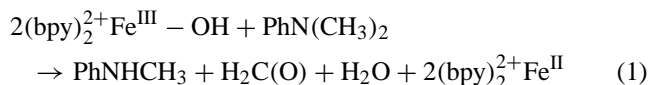
cyclic-voltammograms the reduction peak at +0.72 V (versus, SCE) - or at +0.60 V in the presence of bpy - appears regardless of the presence of bpy in the system (Fig. 5). It is characteristic that the height of the peak increases directly from the rest potential, without an existence of a residual current. If anodic scan is performed first the small, broad anodic peak also arising from the rest potential is observed.

All applied substrates: *N,N*-dimethylaniline, *N*-methylaniline, *N,N*-diethylaniline, and *N*-ethylaniline are electrochemically oxidizable, the shapes of their CV-peaks are the same and their oxidation potentials are very similar and equal to: +0.90, +0.90, +0.95, and +0.80 V, respectively.

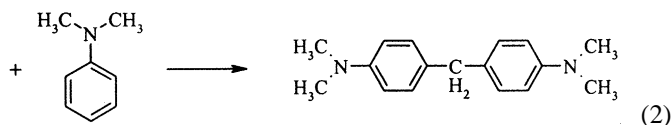
#### 4. Discussion

The results presented indicate that the substrate - *N,N*-dimethylaniline - reduces  $[\text{Fe}^{\text{III}}(\text{H}_2\text{O})_6]_{\text{MeCN}}^{3+}$  and  $[\text{Fe}^{\text{III}}(\text{bpy})_2]_{\text{MeCN}}^{3+}$  to corresponding Fe(II) complexes. The reduction of iron(III) complexes by alkylated amines was previously observed [8d] and demethylation of tertiary amines to secondary amines by potassium hexacyanoferrate(III) in the presence of a base is long-time known reaction [16]. Moreover,  $[\text{Fe}^{\text{III}}(1,10\text{-phenanthroline})_3]^{3+}$  complex and  $\text{Fe}(\text{ClO}_4)_3$  in aprotic solvents are known as a one-electron oxidants, which generates a series of cation-radicals from hydrocarbons [17]. In a recent paper we have reported that Fe(III) catalysts are reduced by cyclohexene during its iron-induced oxygenation by dioxygen in acetonitrile [10]. These facts indicate that in the presence of the large excess of *N,N*-dimethylaniline (like in the reaction conditions applied in the paper), iron catalysts remains in the reduced state, even in the presence of dioxygen. On the basis of present results and those from related studies [8c,10,11,18], and taking into account properties and iron(III) aqua-complexes [19] (we cannot avoid traces of water in acetonitrile) we can postulate that in the absence of dioxygen only  $(\text{bpy})_2^+ \text{Fe}^{\text{III}}\text{-OH}$  species is reactive

with *N,N*-dimethylaniline to produce *N*-methylaniline and formaldehyde in a stoichiometric reaction:



The process occurs according to 2:1 (iron to substrate) stoichiometry. However, the condensation reaction between *N,N*-dimethylaniline (DMA) and formaldehyde to produce 4,4'-methylenebis(*N,N*-dimethylaniline) occurs at the comparable rate to demethylation reaction, which follows from the concentration profiles (Fig. 1). The occurrence of the condensation process (Eq. (2))

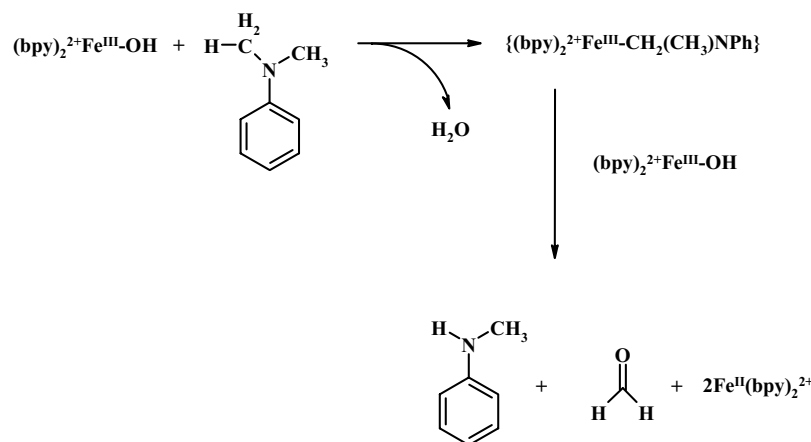


causes that the overall stoichiometry of the reaction between Fe(III) and *N,N*-dimethylaniline is equal to 2:3.

Cyclic-voltammetric measurements show that for the molar combinations of Fe(III) to the substrate from 2:1 to 1:2 the oxidation peak of DMA is absent. However, the product of the reaction - *N*-methylaniline - should be visible, it is also oxidizable at +0.90 V like DMA. The absence of substrate or products oxidation peaks after reaction indicates that the Fe(II) formed interacts with the MA (it was confirmed by independent CV-measurements of Fe(II)/MA system), which also causes the Fe(II) oxidation peak to be shifted towards negative potentials. These possible interactions explain the existence of described effects up to 1:2 molar ratio of iron to the substrate.

In acetonitrile in the presence of a base Fe(III) can abstract hydrogen atom from alkyl C-H bond [8d,10,17,18]. Therefore, in the initial step of the reaction (1) the C-H bond of methylene group is broken with formation of water molecule. The total bond breakage energy for reaction (1) is the sum of C-H bond breakage in *N,N*-dimethylaniline ( $\text{H-CH}_2(\text{CH}_3)\text{NPh}$ ,  $\Delta H_{\text{DBE}} = 352 \text{ kJ mol}^{-1}$ , by analogy to  $\text{H-CH}_2\text{N}(\text{CH}_3)_3$  [20]) and Fe-OH bond in  $(\text{bpy})_2^+ \text{Fe}^{\text{III}}\text{-OH}$  ( $\Delta H_{\text{DBE}} = 222 \text{ kJ mol}^{-1}$  [21]) to form water molecule. Because the total bond-breakage energy ( $\Delta H_{\text{DBE}} = 352 + 222 = 574 \text{ kJ mol}^{-1}$ ) is greater than the free-energy of bond-formation for the HO-H bond ( $-\Delta G_{\text{BF}} = 465 \text{ kJ mol}^{-1}$  [21a]), for the observed process (Eq. (1)) to occur at reasonable rates requires formation of an intermediate with an iron-carbon bond  $\{(\text{bpy})_2^+ \text{Fe}^{\text{III}}\text{CH}_2\text{N}(\text{CH}_3)\text{Ph}\}$ ;  $-\Delta G_{\text{BF}} \sim 110 \text{ kJ mol}^{-1}$  [21b]. The latter will react at diffusion-controlled rates with a second  $(\text{bpy})_2^+ \text{Fe}^{\text{III}}\text{OH}$  to give the observed demethylation products (Scheme 1).

The results obtained indicate that Fe(III) complexes are reduced by the substrate and Fe(II) is responsible for dioxygen activation. The CV-measurements show that the peak of Fe(II) oxidation in the presence of DMA is shifted towards negative potentials, which gives evidence that an



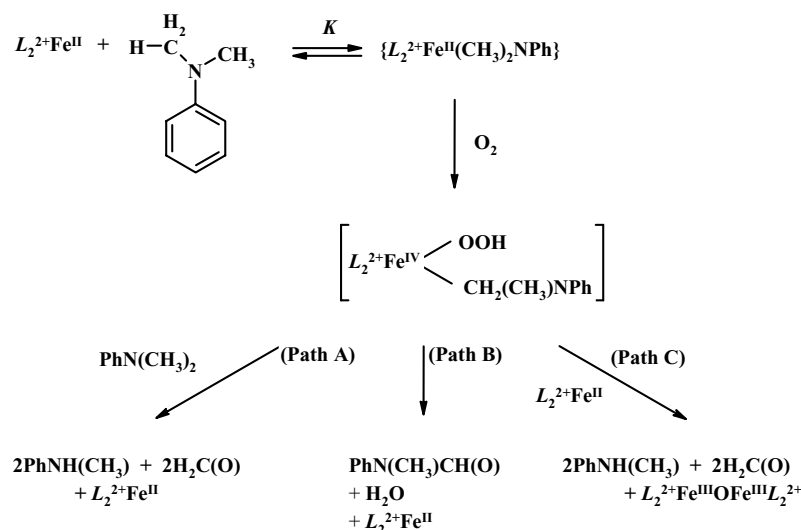
Scheme 1. Proposed mechanism for *N,N*-dimethylaniline oxidation by iron(III) in the absence of dioxygen.

interaction between the iron catalyst and substrate occurs. The described in [15b] process of ligand exchange in the Fe/bpy system in acetonitrile supports the assumption that Fe(II) interacts with the substrate even in the presence of bpy. In experimental part the evidences were shown that the reaction order with respect to dioxygen is less than 1. This situation occurs when an equilibrium step between substrate and catalyst precedes the addition of dioxygen [22].

Based on these facts and previously published results [10,11,18] the proposed putative mechanism, which includes the activation of dioxygen and the substrate, is outlined in Scheme 2. The reactive species  $\{L_2^{2+}Fe^{IV}(OOH)(CH_2(CH_3)NPh)\}$  is a hypothetical one and was proposed on the basis of the results obtained for metal-induced oxygenation of organic substrates in basic, nonaqueous solutions [10,18]. Similar reactive intermediate was postulated in the models of hydrogen peroxide activation [23]. Moreover, several analogous hydroperoxo complexes of iron have been recently isolated and characterized [24].

The proposed intermediate can: (a) react with another substrate to form demethylated product, formaldehyde, and Fe(II) (path A); (b) undergoes decomposition to formanilide derivative, water, and the Fe(II) catalyst (path B); (c) reacts with iron(II) catalyst to produce demethylated product, formaldehyde, and  $\alpha$ -oxo diiron(III) species, which often is the final products of Fe(II) oxidation (path C).

The mechanism is consistent with the results obtained. It is also coherent with the recently introduced proposition of the direct oxygen atom transfer from metal-dioxygen adduct to the  $\alpha$  C–H bond in amine molecule in the concerted insertion mechanism [5z]. The mechanism elucidates the observed fact that the amounts of *N*-methylformanilide formed is always much smaller than *N*-methylaniline - the large concentration of substrate favors the path A. The effect however, is less visible for the 1 mM  $[Fe^{II}(bpy)_2]_{MeCN}^{2+}$ /dioxygen or air systems. Clearly the presence of bpy as a ligand at low catalyst concentrations causes the increase of the efficiency of path B. At the higher catalyst concentration the decrease



Scheme 2. Proposed mechanism for iron(II)-activation of dioxygen for oxygenation of *N,N*-dimethylaniline.

of the reaction yield is observed - in this case path C is more efficient and it leads to catalyst decomposition.

The interesting fact described in the paper is the existence a chromophore at  $\lambda_{\max} = 465$  nm, which is formed only with Fe(III) [not Fe(II)] and DMA, when the concentration the last one not exceed 3 molar equivalents with respect to Fe(III). The species cannot be attributed to a Fe(II)/DMA complex because the oxidation peak of Fe(II)/DMA formed after mixing Fe(III) with DMA (Fig. 2a, curve 3) is present also when the chromophore is not visible. The observed absorption band can be attributed to a  $\mu$ -oxo dimer having a structure  $[L_xFe^{III}OFe^{III}L_x]^{4+}$ , where  $L$  represents DMA and/or bpy and a solvent ( $H_2O$  or MeCN). It is known that Fe(III) in the presence of traces of water shows the tendency to hydrolyze and/or to form complexes [19,25]. One of the major species formed is the  $\mu$ -oxo dimer. It can also activate dioxygen, however its catalytic activity is lower than that for monomeric species [25c]. The excess of DMA as a base and also complexing agent can prevent the formation of the products of hydrolysis, therefore the chromophore is not visible in the condition. However, in the presence of equimolar amounts of  $H^+$  with respect to DMA the same chromophore is visible for higher Fe(III)/DMA molar ratios. This is probably due to the fact that the presence of protons in the solution can promote ligands exchange, as described in [15b] and favor the formation of the species. The species can undergo additional reactions, which includes further hydrolysis [26], ligand exchange, and reduction by DMA, which leads to its disappearance. The cathodic peak observed on the CV-curve at +0.72 V (or at +0.60 V in the presence of bpy) is visible only when the discussed absorption band is present can be attributed to the reduction of the  $\mu$ -oxo dimer. The irreversible electrochemical reduction of  $[Fe_2^{III,III}OL_4S_2]^{4+}$  dimer [ $L =$  bpy or (-)-4,5-pinene-bpy;  $S = H_2O$  or MeCN] is reported [15b]. It is interesting that the reduction peak starts directly from the rest potential, and also the small anodic peak arises directly from the rest potential. Probably in the experimental conditions the formation of a small amounts of mixed valence  $\mu$ -oxo complex  $[L_xFe^{II}OFe^{III}L_x]^{3+}$ , is possible as well, and its oxidation is observed. The possibility of formation of such complexes was also reported in [15b].

The described results show that the system is very labile even in the presence of bpy as a ligand and it is difficult to formulate the nature of the reactive species. However, the results confirm that Fe(III) is reduced by the substrate to Fe(II), which interacts with substrate and activates dioxygen for demethylation process.

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