Activation of molecular oxygen by iron nitrosyls in the presence of bidentate nitrogen ligands (2,2′-bipyridine, 4,4′-dimethyl-2,2′-bipyridine and 1,10-phenanthroline)

Henri Li Kam Wah, Michele Postel*, Felix Tomi
Laboratoire de Chimie Moléculaire, Unité Associée au C.N.R.S. No. 426, Université de Nice, 06108 Nice Cédex 2 (France)
Francine Agbossou, Danielle Ballivet-Tkatchenko* and Fabio Urso
Laboratoire de Chimie de Coordination, Unité Propre du C.N.R.S. No. 8241, 205 route de Narbonne, 31077 Toulouse Cédex (France)

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Abstract

Activation of molecular oxygen (1 atm, room temperature) by the nitrosyl dimer $[Fe(NO)_2Cl]_2$ in the presence of the bidentate nitrogen ligands NN (NN = 2,2′-bipyridine (bpy), 4,4-dimethyl-2,2′-bipyridine (Me_2bpy) and 1,10-phenanthroline (phen)) yields the molecular iron nitrates $Fe(NO_3)_2Cl(NN)$ and $Fe(NO_3)Cl_2(NN)$. The same result is obtained when the ionic complexes $[Fe(NN)_3][Fe(NO)_2Cl_2]_2$ are allowed to react with molecular O_2. All these nitrato complexes transfer oxygen to phosphines and catalyse the autoxidation of cyclohexene.

Introduction

The oxidation of organic compounds by molecular oxygen catalysed by transition-metal complexes is attracting considerable attention. Recently, we reported [1, 2] that activation and transfer of molecular oxygen can be achieved through (i) splitting of dioxygen on a nitrosyl ligand coordinated to iron, which, in the presence of phosphorous ligands, results in the exclusive formation of iron nitrates, followed by (ii) oxygen transfer from these nitrates to olefins and phosphines. These Fe–NO/Fe–NO_3 systems have the potential to be developed into the long-sought catalyst for the direct epoxidation of olefins by molecular oxygen.

In our search for the best ligand environment for such a system, we became interested in ligands which are stable under oxidizing conditions and first considered bidentate nitrogen ligands with a high degree of aromaticity. We have already reported the reaction of $[Fe(NO)_2Cl_2]_2$ with amines such as 2,2′-bipyridine, 4,4′-dimethyl-2,2′-bipyridine or 1,10-phenanthroline to obtain the ionic $[Fe(NN)_3][Fe(NO)_2Cl]_2$ species [3]. The next step in our search, which is reported herein, was to determine whether the iron nitrosyl moiety, in the presence of such ligands, was still capable of both activating and transferring molecular oxygen.

Results

Preparation of nitrato iron complexes by O_2 oxidation of nitrosyl ligands

Bubbling oxygen through dichloromethane or acetonitrile solutions of the diamagnetic dimer $[Fe(NO)_2Cl]_2$ (**1**) at room temperature, in the presence of 2 equiv. of the bidentate nitrogen ligands NN (NN = 2,2′-bipyridine (bpy), 4,4′-dimethyl-2,2′-bipyridine (Me_2bpy) and 1,10-phenanthroline (phen)), caused a rapid change in colour of the solution from red–black to yellow–orange and the formation of a brown precipitate. From this latter brown precipitate, which represents *c.* 40% of the starting iron, no definite species could be identified: its IR print showed absorptions at 1516 and 1280 cm^{-1}, *i.e.* assignable to bound nitrates [4], and at 875 cm^{-1} which could arise from a ν(O–O) band [5]. The same orange–yellow solution and brown precipitate were obtained from oxygenation reactions when conducted on solutions of the ionic complexes $[Fe(NN)_3][Fe(NO)_2Cl_2]_2$ (**2a**) (NN = bpy), **2b** (NN = Me_2bpy) and **2c** (NN = phen) which we isolated [3] from the instantaneous reaction, under an argon atmosphere, of **1** and the NN ligands (2 equiv.).

The IR spectra of the crude yellow–orange complexes, obtained from the solution and which account for *c.* 60% of the starting iron, apart from the vibrations characteristic for the coordinated NN ligands, show new bands in the 1560–1510 and 1280–1260 cm^{-1} regions

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*Authors to whom correspondence should be addressed.

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which are generally assigned to bidentate nitrates [4]. An additional vibration, observed at 1380 cm^{-1} and detected only for KBr pellets, is assigned to the free NO_3^- anion due to Br^- anion exchange [6]. In the region of Fe–Cl vibrations, three bands were observed at 380, 360 and 330 cm^{-1}, respectively. Specific analysis of NO_3 and NO_2 groups [7] revealed the presence of only nitrates (absence of even traces of nitrites). In all cases, elemental analyses performed on the product of the reaction indicated the $Fe_2Cl_x(NO_3)_y(NN)_2$ formulation, which can be accounted for by either a mixture of $Fe(NO_3)Cl_2(NN)$ (**3**) and $Fe(NO_3)_2Cl(NN)$ (**4**), or an ionic species of the type $[Fe(NO_3)_y(Cl)_x]$-$[Fe(NO_3)_{3-y}(Cl)_{3-x}NN]$. As conductivity measurements showed that the product (or mixture of products) obtained is non-ionic, we propose the simultaneous formation of the mono- and dinitrato complexes **3** and **4**. This hypothesis was confirmed through independent syntheses of both **3** and **4**. These are easily obtained when $FeCl_3(NN)$ (**5**) complexes [8] are allowed to react with 1 or 2 equiv. of $AgNO_3$, respectively. The IR and analytical data of the complexes **3a–c** and **4a–c** are given in Table 1.

The respective solubilities of **3** and **4** depend on the nature of the bidentate nitrogen ligand bpy, Me_2bpy or phen so that, by recrystallization at 4 °C of the nitrate mixture obtained by reaction of **1** with O_2 in the presence of NN, in dichloromethane/heptane (1/1), crystals of $Fe(NO_3)Cl_2(Me_2bpy)$ (**3b**), $Fe(NO_3)$-$Cl_2(phen)$ (**3c**), or $Fe(NO_3)_2Cl(bpy)$ (**4a**) were obtained.

Oxygen transfer from the iron nitrato complexes 3 and 4

The nitrato complexes **3** and **4** were all found to be most reluctant to react stoichiometrically with olefins under anaerobic conditions. No reaction was observed between **3** or **4** and cyclohexene (olefin/Fe = 10/1) after 72 h at room temperature under argon. The unaltered nitrato complexes were quantitatively recovered.

On the other hand, **3** and **4** react rapidly with phosphines in the absence of oxygen. Thus, when the nitrato complexes **3** or **4**, in CH_2Cl_2 or CH_3CN solutions, are allowed to react with PPh_3 (tenfold excess) under argon at room temperature, a change of colour from yellow to deep-red is instantaneously observed. IR monitoring of the reaction shows the rapid disappearance of the NO_3 vibrations together with the appearance of bands due to $OPPh_3$ (ν(P=O) = 1188 cm^{-1}) and NO ligand (ν(NO) = 1760 cm^{-1}). Besides the formation of $OPPh_3$, the reaction gives a mixture of iron complexes which we could not isolate for further characterization. However, the presence of a ν(NO) vibration in the IR print of the iron residue of the reaction, is interpreted to indicate that the oxygen transfer from **3** or **4** to PPh_3 involves the NO_3–NO transformation.

Complexes 2, 3 and 4 as catalysts in cyclohexene oxidation

The various nitrosyl **2a–c** and nitrato **3a–c**, **4a–c** complexes catalyse the aerobic oxidation of cyclohexene to mainly 2-cyclohexene-1-one and 2-cyclohexene-1-ol; cyclohexeneoxide is formed in up to 7% amounts (Table 2). In the case of the dichloroiron nitrates **3**, 3-chlorocyclohexene (*c.* 1%) is also formed. These organic products were identified by GC-MS and their spectra compared with those of authentic samples.

It is noteworthy that $[Fe(NO)_2Cl_2]^-$ (**6**) is also a catalyst in this reaction while, on the other hand, the $[Fe(NN)_3]^{2+}$ cations, taken as the dichlorides, were found to be inactive.

The alkene conversion and the distribution of the reaction products were found to depend upon the solvent (Table 2). The reaction was carried out either in acetonitrile or in dichloromethane. In dichloromethane, compound **6** is more active than the mono- and dinitrato complexes **3** and **4** for which, on the other hand, less active systems are found going from bpy, Me_2bpy to phen. Such a classification is not found in acetonitrile which, on the other hand, led to better conversions and to a higher selectivity for 2-cyclohexene-1-one. Among all the systems studied in this work, the highest conversion is obtained in the presence of **4a** in acetonitrile together with the highest selectivity for the ketone: 2-cyclohexene-1-one (74%), 2-cyclohexene-1-ol (19%), cyclohexeneoxide (7%).

Discussion

Activation of oxygen: nitrato versus nitro formation

Our results show that the reaction of molecular oxygen with the iron nitrosyl dimer **1**, in the presence of NN ligands, is quite intricate and produces a complex mixture of compounds from which the mono- and dinitrato complexes, **3a** and **4a**, respectively, could be isolated; they account for *c.* 60% of the starting iron.

We have shown that, in the presence of the same NN ligands, the $[Fe(NO)_2Cl]_2$ dimer yields $[Fe(NN)_3][Fe(NO)_2Cl_2]$ [3]. Its oxidation by molecular oxygen also produces a mixture of the same species. Therefore the mechanism implies several steps with ligand redistribution.

This is in marked contrast with the clean and selective reaction that we have found in the presence of PPh_3 (or $OPPh_3$) [1]: the oxygenation of the $[Fe(NO)_2Cl]_2$ dimer (or of the $Fe(NO)_2Cl(PPh_3)$ molecular complex) almost quantitatively yields the $Fe(NO_3)Cl(OPPh_3)_2$ dinitrate. The complex behaviour of the iron nitrosyl

E 1. Elemental analyses and IR data on compounds **3–6**

ex	Analysis: Found (calc.) (%)					Infrared (cm^{-1}; KBr p	
	C	H	N	Cl	Fe	NO_3	Fe
NO_3)(bpy) **(3a)**	34.40 (34.82)	2.31 (2.34)	12.03 (12.18)	21.03 (20.56)	16.22 (16.19)	1540 1524 1277	37 33
NO_3)(Me_2bpy) **(3b)**	38.61 (38.64)	3.19 (3.24)	11.39 (11.17)	17.64 (19.01)		1553 1531 1269	38 33
NO_3)(phen) **(3c)**	39.41 (39.06)	2.39 (2.19)	10.59 (11.39)	20.78 (19.22)	14.55 (15.14)	1558 1520 1273	38 33
$NO_3)_2$(bpy) **(4a)**	32.36 (32.33)	2.26 (2.17)	15.02 (15.08)	9.21 (9.54)		1540 1524 1273	36
$NO_3)_2$(Me_2bpy) **(4b)**	36.27 (36.07)	3.01 (3.03)	14.11 (14.02)	8.69 (8.87)	14.00 (13.98)	1544 1531 1273	36
$NO_3)_2$(phen) **(4c)**	36.55 (36.44)	1.92 (2.04)	14.27 (14.17)	8.98 (8.96)	14.15 (14.12)	1537 1522 1261	35
bpy) **(5a)**	38.08 (37.72)	2.54 (2.53)	8.80 (8.80)	33.14 (33.40)			37 33
Me_2bpy) **(5b)**	41.95 (41.60)	3.48 (3.49)	8.08 (8.09)				38 33
phen) **(5c)**	42.10 (42.09)	2.63 (2.36)	8.28 (8.18)				37 33
$O)_2Cl_2][Ph_4As]$ **(6)**	50.81 (50.56)	3.61 (3.54)	4.60 (4.91)	12.31 (12.44)	9.03 (9.80)		35 32

TABLE 2. O_2 oxidation of cyclohexene catalysed by iron nitrosyl and iron nitrato complexes at room temperature after 72 h[a]

Complex	Solvent	Distribution of the oxygenated products (%)			Alkene conversion (%)
		epoxide	alcohol	ketone	
2a	CH_2Cl_2	6	39	55	18
	CH_3CN	5	25	70	53
2b	CH_2Cl_2	3	46	51	15
	CH_3CN	4	21	72	66
2c	CH_2Cl_2	3	43	54	16
	CH_3CN	4	28	68	59
3a	CH_2Cl_2	3	44	53	35
	CH_3CN	3	32	65	50
3b	CH_2Cl_2	3	45	52	21
	CH_3CN	6	26	68	66
3c	CH_2Cl_2	3	50	47	13
	CH_3CN	2	32	66	44
4a	CH_2Cl_2	3	42	55	35
	CH_3CN	7	19	74	76
4b	CH_2Cl_2	2	55	43	24
	CH_3CN	2	37	61	44
4c	CH_2Cl_2	3	52	45	7
	CH_3CN	5	22	73	58
6	CH_2Cl_2	3	45	52	34
	CH_3CN	3	35	61	52

[a]Reaction conditions: O_2 (1 atm); $[Fe]=2\times10^{-2}$ M; [cyclohexene]/[complex] = 100.

dimer in the presence of NN is most likely to be related to the formation of compounds **2**. While we found $[Fe(NN)_3]^{2+}$ to be most reluctant to react with O_2, $[Fe(NO)_2Cl_2]^-$ is rapidly degraded under oxygen.

The formation of covalently bound nitrate has previously been reported. According to the starting complexes different intermediates were characterized. Dioxygen complexes were found to be involved with four-coordinated d^{10}ruthenium dinitrosyl species [5] whereas the oxidation reaction with $[RuCl(NO)(bpy)_2]^{2+}$ proceeds through the formation of a Ru(III) nitro complex, $[RuCl(NO_2)(bpy)_2]^+$, long thought to exist only as a kinetic transient which was finally isolated under basic conditions [9–11]. Other examples with Co(L)NO complexes (L = Schiff base or oxime chelate) in the presence of a Lewis base [12, 13] show that oxygen would most likely form a peroxynitrite intermediate NOO_2 which, upon further rearrangement, produces nitro species in the presence of Schiff base or a mixture of nitro and nitrato complexes with the oxime. The factors governing the subsequent reaction of the peroxynitrite have not been identified. Recently it has been proposed that nitrato species will be formed if the nitrosyl ligand has some NO^- character [14].

A probable first step in the oxygenation of **2** (or **1** in the presence of NN) could correspond to oxygen attack on the 17-electron $[Fe(NO)_2Cl_2]^-$ anion resulting in O_2 substitution for either NO or Cl. Another possible route could be through a peroxynitrite formation $[Fe(NOO_2)(NO)Cl_2]^-$ which could undergo rearrangement to the nitrosylnitrato derivative $[Fe(NO_3)(NO)Cl_2]^-$.

Oxidation reactions: mechanistic approach

It has been reported that molecular oxygen can oxidize NO ligands bound to palladium or rhodium, into NO_2 ligands and that the resulting redox couples are able to catalyse the O atom transfer from the nitro ligand to an olefin [15]. The role of the metal centre is to promote olefin activation and the preferred intermediate is a metallacycle either with mononuclear or bimetallic systems. With these systems, olefins are preferentially oxidized into the corresponding saturated ketone [16, 17].

In our work, the main product is the α,β-unsaturated ketone showing that allylic oxidation is the main process. When cyclohexene is the substrate, 2-cyclohexene-1-one, 2-cyclohexene-1-ol and cyclohexeneoxide are formed in a 70:25:5 ratio. The selectivity is characteristic of cyclohexene autoxidation [18–20]. Such allylic oxidation of alkenes by molecular oxygen in the presence of transition-metal complexes has been known for a long time [21].

In order to establish the radical nature of the oxidation process, several tests have been carried out. The oxidation of cyclohexene was found to be severely inhibited when a radical trap, *via* 2,6-diterbutyl-4-methylphenol, was added to the reaction mixture in both acetonitrile and dichloromethane for **3a** and **4a**; the oxidation reaction is slowed down when the radical trap/iron complex ratio increases and is totally stopped when this ratio is higher than 2. Changing cyclohexene for α-methylstyrene as the substrate, the only product was acetophenone (selectivity $>95\%$ as determined by GC), the typical product of autoxidation [19]. Norbornene and 3-cyclohexene-1-ol were found to be unreactive.

Additionally, when we reacted cyclohexene with tert-butylhydroperoxide, in the presence of $\{Fe(NO)_2Cl\}_2$ (**1**) and bipy (1:2) in acetonitrile at room temperature under anaerobic conditions, cyclohexenylbutylhydroperoxide, 2-cyclohexene-1-one and 2-cyclohexene-1-ol were formed in a 71:23:6 ratio after 72 h, while no cyclohexeneoxide was detected. This indicates that the iron complex was inactive for the decomposition of the cyclohexenyltertiobutylperoxide.

These experiments show that the main oxidation pathway by molecular oxygen involves a radical mechanism with formation of a hydroperoxide and its further homolytic decomposition induced by the metal centre. The oxidation of the nitrosyl ligand into a nitrato instead of a nitro group is presumably at the origin of this mechanism since the resulting oxidation state of the iron centre is +3. It is noteworthy that Fenton's reagent, consisting of a combination of iron(II) and hydrogen peroxide, effects the hydroxylation of organic substrates via a free radical chain process where iron(III) and oxo iron(IV) species seem to be involved [22].

In an attempt to favour the NO/NO_2 redox couple, we changed the nature of the metal, *via* iron for cobalt. Under the same experimental conditions, in the presence of two py or one bpy (phen) ligands in aerobic conditions with cyclohexene, the $[Co(NO)_2Cl]_2$ complex was inactive although NO was oxidized into NO_2. However, NO_2 was not a good ligand for the cobalt complex and was detected in the gas phase. The same result was obtained starting from the cationic $[Co(NO)_2(MeCN)_2]^+$ complex [23].

Experimental

General procedures

All experiments were carried out under argon or oxygen atmosphere using Schlenk tube techniques. Reagent grade solvents were purified by published procedures and stored under argon. The ligands 2,2′-bipyridine, 4,4′-dimethyl-2,2′-bipyridine and 1,10-phenanthroline were obtained from Fluka and recrystallized from petroleum ether. The dimer $[Fe(NO)_2Cl]_2$ (**1**) [24] and the ionic complexes **2a–c** [3] were prepared according to the literature. IR spectra were obtained as KBr pellets on a Bruker FT-IFS 45 spectrometer. Conductivity measurements were obtained with a Tacussel CDN 6 conductimeter. Elemental analyses were performed by the Service Central d'Analyses of the CNRS.

*$Fe(NO_3)Cl_2(Me_2bpy)$ (**3b**) from **2b***

Oxygen was bubbled into a stirred dark-red solution of **2b** (1.05 g, 1.07 mmol) in dichloromethane (50 ml). A change of colour to orange–red and formation of a red precipitate were observed after 5 min. After filtration and evaporation, an orange–yellow powder resulted which, by recrystallization in mixtures of dichloromethane/heptane 1:1, afforded amber hexagonal crystals of **3b** (0.11 g, 9% yield based on iron).

*$Fe(NO_3)Cl_2(phen)$ (**3c**)*

2.303 g of phen·H_2O (11.6 mmol) were added to a solution of the iron dimer (1.76 g, 5.81 mmol) in 100 ml of dichloromethane. A change of colour to deep red was observed. Oxygen was then bubbled into the solution, resulting in an immediate change of colour to orange–yellow. After filtration and evaporation, the solid obtained (2.51 g) was washed with 40 ml of diethyl ether before being dried under vacuum. By recrystallization from a dichloromethane/heptane 1:1 mixture, amber crystals of **3c** were obtained (0.91 g, 14% yield based on iron).

*$FeCl_2(NO_3)(bpy)$ (**3a**), $FeCl(NO_3)_2(bpy)$ (**4a**), $FeCl_2(NO_3)(Me_2bpy)$ (**3b**), $FeCl(NO_3)_2(Me_2bpy)$ (**4b**), $FeCl_2(NO_3)(phen)$ (**3c**) and $FeCl(NO_3)_2(phen)$ **4c**)*

To a stirred yellowish-brown solution of **5a** (1.389 g, 4.30 mmol) in acetonitrile (75 ml) was added solid $AgNO_3$ (0.73 g, 4.30 mmol). The solution became yellower and a white precipitate formed. After 1 h, the precipitated AgCl (0.59 g, 4.1 mmol) was removed by filtration and the solution allowed to stand for 3 days at 0 °C. Yellow crystals of **3a** were obtained. Yield 1.33 g, 90%.

The same procedure was applied for the preparations of **4a**, **3b**, **4b**, **3c** and **4c**.

3b: 0.248 g of **5b** (0.72 mmol), 0.122 g of $AgNO_3$ (0.72 mmol); yield 0.24 g, 89%.

3c: 0.64 g of **5c** (1.87 mmol), 0.138 g of $AgNO_3$ (1.87 mmol); yield 0.460 g, 67%.

4a: 0.623 g of **5a** (1.96 mmol), 0.665 g of $AgNO_3$ (3.91 mmol); yield 0.66 g, 91%.

4b: 0.66 g of **5b** (1.91 mmol), 0.647 g of $AgNO_3$ (3.81 mmol); yield 0.618 g, 87%.

4c: 1.233 g of **5c** (3.60 mmol), 1.227 g of $AgNO_3$ (7.22 mmol); yield 1.21 g, 85%.

Fe(bpy)Cl$_3$ (5a), Fe(Me$_2$bpy)Cl$_3$ (5b) and Fe(phen)Cl$_3$ (5c)

To a stirred reddish-yellow solution of anhydrous iron(III) chloride (2.80 g, 17.26 mmol) in acetonitrile (25 ml) was added bipyridine (2.73 g, 17.48 mmol). The solution instantaneously became yellow–brown. By slow evaporation, transparent yellow–brown crystals of $Fe(bpy)Cl_3$ (**5a**) were obtained after one day. Yield 5.16 g, 94%.

The same procedure was applied for the preparation of $Fe(Me_2bpy)Cl_3$ (**5b**) ($FeCl_3$: 2.47 g, 15.2 mmol; Me_2bpy: 2.81 g, 15.3 mmol; yield 4.61 g, 88%) and $Fe(phen)Cl_3$ (**5c**) ($FeCl_3$: 1.37 g, 8.45 mmol; $phen \cdot H_2O$: 1.675 g, 8.45 mmol; yield 2.89 g, 91%).

[Fe(NO)$_2$Cl$_2$][Ph$_4$As] (6)

To 0.20 g (0.87 mmol) of **1** in toluene (25 ml), 0.70 g (1.80 mmol) of Ph_4AsCl was added to immediately form a grey precipitate. This was filtered and dried under vacuum to give 0.83 g (1.45 mmol) of **6** (84%).

General procedure for the oxidation tests

The iron complexes (0.1 mmol) were dissolved in 5 ml of CH_2Cl_2 or CH_3CN, and cyclohexene (10 mmol) was added to the solution together with n-octane as an internal standard for GC analyses. Gas phase analysis was performed with a DELSI 300 chromatograph (katharometric detection) on a SE 30 stainless steel (3 m) column. The resulting solution was stirred under an atmosphere of oxygen at room temperature and the formation of oxidation products monitored by GC analysis of aliquot samples. The oxygenated products were identified by GC-MS coupling by comparison with authentic samples.

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