N-Hydroxyphthalimide: A Hydrogen Atom Transfer Mediator in Hydrocarbon Oxidations Promoted by Nonheme Iron(IV)−Oxo Complexes

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S Supporting Information

ABSTRACT: The oxidation of a series of hydrocarbons by the nonheme iron(IV)−oxo complex $[(N4Py)Fe^{IV}=O]^{2+}$ is efficiently mediated by *N*-hydroxyphthalimide. The increase of reactivity is associated to the oxidation of the mediator to the phthalimide *N*-oxyl radical, which efficiently abstracts a hydrogen atom from the substrates, regenerating the mediator in its reduced form.
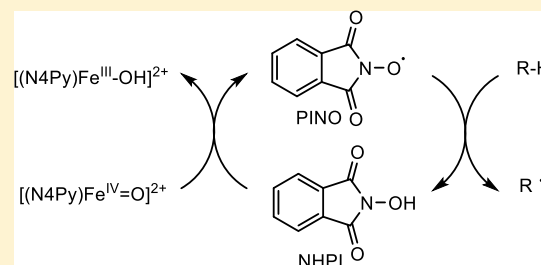
INTRODUCTION

Oxidation processes mediated by *N*-hydroxy derivatives, and in particular *N*-hydroxyphthalimide (NHPI), have attracted widespread research attention in recent years. NHPI activation by several oxidizing species, metal-based or nonmetallic such as nitric oxides, quinones, and peroxyacids, leads to the formation of the phthalimide-*N*-oxyl (PINO) radical, which after a hydrogen atom transfer (HAT) process from organic substrates regenerates NHPI, propagating the oxidative cycle (Scheme 1).[1]

Scheme 1. Activation of NHPI and Hydrogen Atom Transfer from an Organic Substrate
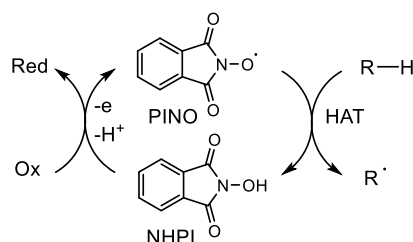
Among these systems, an explicit role of NHPI as mediator has been described, in particular, in two specific examples. In the former, NHPI has been used as redox mediator in the aerobic oxidative functionalization of organic compounds promoted by laccase,[2] a multicopper oxidase enzyme active in the delignification of wood.[3] Following monoelectronic oxidation by the Cu(II) form of the enzyme, the oxidized mediator PINO is formed, which diffuses into the woody fibers and delivers oxidative equivalents to appropriate functional groups of the lignin polymer, and in particular the nonphenolic functions, promoting their oxidation by a HAT process, not available to laccase (Scheme 2). This way the mediator expands the oxidation ability of the enzyme.[4]

NHPI plays also an important role as redox mediator in the absence of chemical oxidants under electrochemical conditions. PINO and other short-lived *N*-oxyl radicals can be easily generated at the electrode surface after electron removal and deprotonation of the corresponding *N*-hydroxy derivatives,[5] enabling them to mediate a number of electrosynthetic organic transformations (Scheme 3) such as alcohol oxidation, where NHPI-mediated electrochemical reactions proceed by rate-limiting HAT from α-C−H bonds to PINO, finally leading to carbonyl products.[6] Electrochemical oxygenation of hydrocarbons has been also reported with activated substrates containing weak C−H bonds (benzylic, allylic, or α to heteroatom).[7]

The use of redox mediators such as NHPI may be profitably extended to the oxidations catalyzed by nonheme amino-pyridine iron complexes, which are biomimetic models of natural nonheme iron oxygenases.[8] Activation of these iron complexes with H_2O_2, and other oxidants such as PhIO, peroxyacids, and alkyl peroxides, catalytically generates a number of iron−oxo or iron−peroxo species, which are able to promote several oxidative processes such as hydroxylation of aliphatic and aromatic compounds, alcohol oxidation, sulfide, and amine oxidation.[8,9] The nature of the active species responsible of the oxidative process depends on the ligand structure, type of oxidant, and reaction conditions employed in the catalytic process.

Several studies have been carried out on the reactivity of iron(IV)−oxo complexes because of the relatively high stability of these species. One of the most thoroughly studied

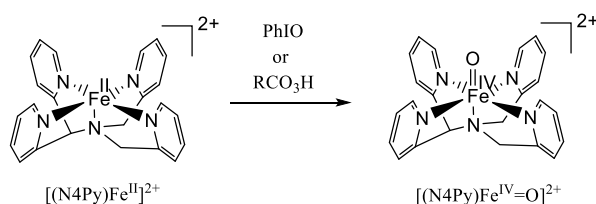**Scheme 2. Catalytic Cycle for the Oxidation of Nonphenolic Benzylic Functional Groups by the Laccase/Mediator (NHPI)/O$_2$ System**
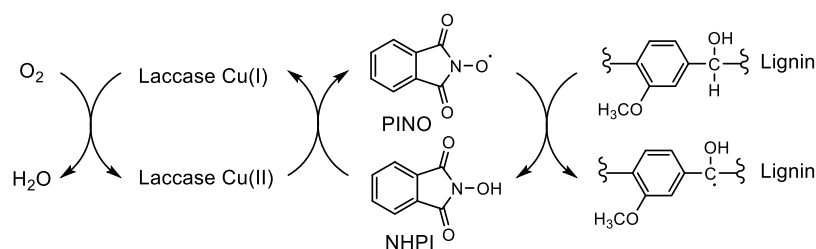
Scheme 3. Electrooxidations of Organic Compounds Mediated by NHPI

Scheme 4. NHPI-Mediated Oxidation of Organic Compounds Promoted by [(N4Py)Fe^{IV}=O]$^{2+}$
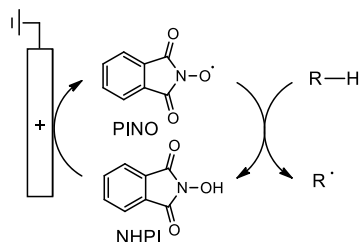
iron(IV)−oxo complex is [(N4Py)Fe^{IV}=O]$^{2+}$ [N4Py = *N,N*-bis(2-pyridylmethyl)-*N*-bis(2-pyridyl)methylamine], which is generated by the oxidation of complex [(N4Py)Fe^{II}]$^{2+}$ with oxygen atom transfer agents such as iodosylbenzene or peroxyacids (Figure 1).[10−19]
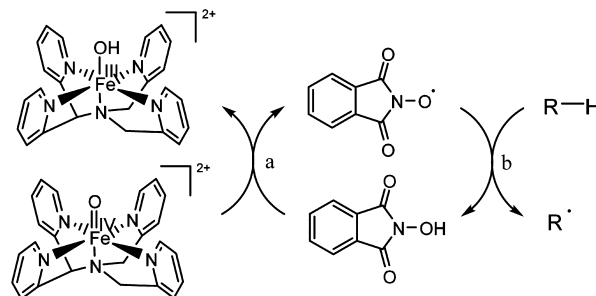

Figure 1. Generation of a nonheme iron(IV)−oxo complex [(N4Py)Fe^{IV}=O]$^{2+}$.

withdrawing (4-NO$_2$, 4-CO$_2$CH$_3$, 3-F) or electron-donating groups (4-CH$_3$, 4-CH$_3$O) (Figure 2).[21−26]
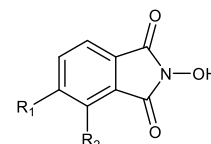
1a	R$_1$= NO$_2$	R$_2$=H
1b	R$_1$= CO$_2$CH$_3$	R$_2$=H
1c	R$_1$= H	R$_2$=F
1d	R$_1$= H	R$_2$=H
1e	R$_1$= CH$_3$	R$_2$=H
1f	R$_1$= OCH$_3$	R$_2$=H

Figure 2. Aryl-substituted NHPIs used as mediators.

The high stability of these species is generally associated to a relatively low intrinsic reactivity, which limits their possible application to the oxidation of less-reactive substrates such as aliphatic hydrocarbons containing strong C−H bonds.

On this basis, we have considered it worthwhile to test whether NHPI may act as a mediator in the oxidation of hydrocarbons by nonheme iron(IV)−oxo complexes enhancing their reactivity and expanding their oxidizing ability (Scheme 4). It is worth noting that NHPI acts as an efficient co-catalyst in alcohol oxidation by *t*-BuOOH catalyzed by the two nonheme iron catalysts [Fe(bpc)Cl$_2$][Et$_4$N] and [Fe(Me$_2$bpb)Cl$_2$][Et$_3$NH] and that a key role played by PINO in the catalytic systems has been recently proposed by Kim and co-workers.[20]

We report herein a detailed kinetic and product study of the oxidation of a series of hydrocarbons (triphenylmethane, toluene, ethylbenzene, and cyclohexane) by the nonheme iron(IV)−oxo complex [(N4Py)Fe^{IV}=O]$^{2+}$ in CH$_3$CN mediated by NHPI.

The electronic effects of aryl substituents on the mediation efficiency have also been evaluated using a series of aryl-substituted NHPIs as mediators containing either electron-

■ RESULTS AND DISCUSSION

The rapid oxidation of *N*-hydroxyimide mediators (X−NHPIs) to the corresponding *N*-oxyl radicals (X−PINOs) promoted by [(N4Py)Fe^{IV}=O]$^{2+}$ (path a in Scheme 4) is a fundamental requirement for their action as redox mediators. Thus, we have started our investigation of the potential use of X−NHPI mediators by analyzing the oxidation of aryl-substituted NHPIs with [(N4Py)Fe^{IV}=O]$^{2+}$. To this purpose, a solution of [(N4Py)Fe^{IV}=O]$^{2+}$ (1.5 mM in CH$_3$CN) was prepared by oxidation of the corresponding iron(II) complex [(N4Py)Fe^{II}(OTf)$_2$] with a slight excess of solid PhIO (1.2 equiv).[11] After 30 min, the solution was filtered and 20 mol % of X−NHPI (X = H, 3-F, 4-CH$_3$, 4-OCH$_3$) with respect to [(N4Py)Fe^{IV}=O]$^{2+}$ was added. In all cases, a decrease of ca. 20% of the visible absorption bands of [(N4Py)Fe^{IV}=O]$^{2+}$ (λ_{max} = 695 nm, ε = 400 M^{-1} s^{-1})[12] was observed too fast to follow by a simple spectrophotometric analysis with the exception of the less easily oxidizable 4-NO$_2$−NHPI.[21] The decay of [(N4Py)Fe^{IV}=O]$^{2+}$ is due to the reduction of the oxo complex by the *N*-hydroxy derivatives; accordingly, in the

case of 4-CH$_3$O−NHPI, it was possible to observe the visible band associated to the corresponding N-oxyl radical (4-CH$_3$O−PINO) (Figure 3).[22,27] Formation of N-oxyl radicals
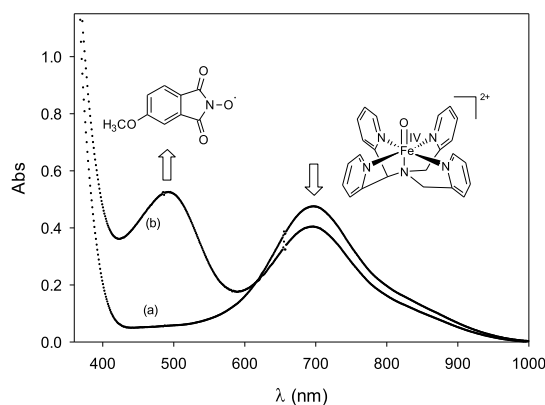

Figure 3. Absorption spectra of the $[(N4Py)Fe^{IV}=O]^{2+}$ (1.5 mM in CH$_3$CN) (a) in the absence of and (b) after addition of 20 mol % of 4-CH$_3$O−NHPI.

absorbing at λ < 400 nm could not be observed because of the overlap with the intense absorption band of the iron complex (see Figures S2−S4 in the Supporting Information). The iron(III)−hydroxo complex $[(N4Py)Fe^{III}−OH]^{2+}$, which has no significant absorption at λ > 400 nm,[28] is not further reduced to $[(N4Py)Fe^{II}]^{2+}$ by X−NHPIs as evidenced by the absence of the characteristic intense absorption band of the latter, centered at 458 nm (ε = 4000 M^{-1} s^{-1} in acetone).[29]

Reaction of $[(N4Py)Fe^{IV}=O]^{2+}$ with the least reactive mediator 4-NO$_2$−NHPI was slow enough to be followed through the absorption decay of $[(N4Py)Fe^{IV}=O]^{2+}$ detected by stopped-flow spectrophotometric analysis. Two solutions of $[(N4Py)Fe^{IV}=O]^{2+}$ (2 mM in CH$_3$CN) and 4-NO$_2$−NHPI (20 mM in CH$_3$CN) were introduced into the reservoirs of the stopped-flow instrument and mixed in a 1:1 volume ratio to obtain final concentrations of 1 and 10 mM for $[(N4Py)Fe^{IV}=O]^{2+}$ and 4-NO$_2$−NHPI, respectively. An exponential first-order decay of $[(N4Py)Fe^{IV}=O]^{2+}$ was observed with a pseudo-first-order rate constant k_{obs} = 0.77 s^{-1} (Figure S5 in the Supporting Information).

Once verified that $[(N4Py)Fe^{IV}=O]^{2+}$ is able to rapidly generate the oxidized form of the X−NHPIs mediators, the $[(N4Py)Fe^{IV}=O]^{2+}$/NHPI system was tested in the C−H oxidation of the benchmark substrate triphenylmethane. Kinetic studies were performed by spectrophotometric analysis as described above for the reaction in the absence of substrate. To a solution of $[(N4Py)Fe^{IV}=O]^{2+}$ (1.5 mM) in CH$_3$CN under nitrogen, NHPI (20 mol % with respect to $[(N4Py)-Fe^{IV}=O]^{2+}$) was added in the cuvette followed by addition of a triphenylmethane solution (final concentration 30 mM). Substrate oxidation was monitored following the decay of the band centered at 690 nm related to $[(N4Py)Fe^{IV}=O]^{2+}$. In the presence of air, no effect was observed on the decay rate of the 690 nm band. As a control experiment, the oxidation of triphenylmethane promoted by $[(N4Py)Fe^{IV}=O]^{2+}$ was carried out in the absence of the mediator under the same reaction conditions. Pleasantly, we observed that the decay of the iron(IV)−oxo complex $[(N4Py)Fe^{IV}=O]^{2+}$ in the absence of NHPI is much slower ($t^0_{1/2}$ = 450 s) than in the presence of the mediator ($t^{med}_{1/2}$ = 33 s)[30] (Figure 4) with a mediation efficiency $t^0_{1/2}/t^{med}_{1/2}$ of 13.6. On increasing the relative amount of the mediator from 5 to 25%, a steady increase of the mediation efficiency was observed (Table 1 and Figures S6−S8 in the Supporting Information), in line with expectations.

Table 1. Decay Half-Life of the Iron(IV)−Oxo Complex $[(N4Py)Fe^{IV}=O]^{2+}$ ($t^{med}_{1/2}$) and Mediation Efficiency ($t^0_{1/2}/t^{med}_{1/2}$) in the Oxidation of Triphenylmethane Promoted by $[(N4Py)Fe^{IV}=O]^{2+}$ (1.5 mM) in the Absence or in the Presence of Varying Amounts of NHPI Mediator in CH$_3$CN

% mediator	$t^{med}_{1/2}$ (s)	mediation efficiency ($t^0_{1/2}/t^{med}_{1/2}$)
0	450 ($t^0_{1/2}$)	
5	110	4.1
10	55	8.2
20	33	13.6
25	22	20.5

The effect of NHPI aryl substituents on the mediation efficiency in the oxidation of triphenylmethane with $[(N4Py)-Fe^{IV}=O]^{2+}$ was also investigated using NHPIs containing either electron-withdrawing (4-NO$_2$, 4-CO$_2$CH$_3$, 3-F) or electron-donating groups (4-CH$_3$, 4-CH$_3$O).
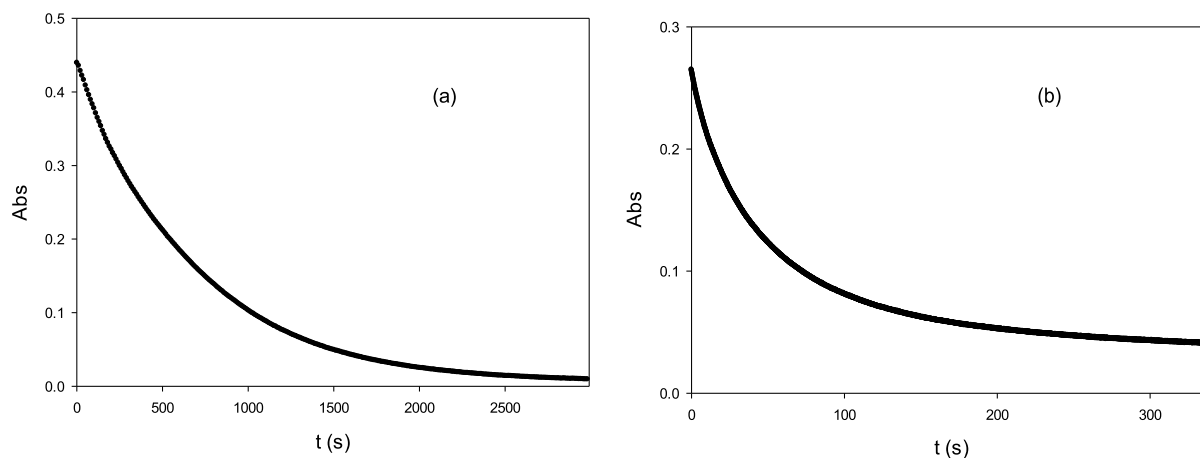

Figure 4. Decay of absorbance recorded at 690 nm in the oxidation of triphenylmethane (30 mM) with $[(N4Py)Fe^{IV}=O]^{2+}$ (1.5 mM) (a) in the absence of and (b) in the presence of 20 mol % of NHPI in CH$_3$CN.

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Kinetic analysis has been performed under the same experimental conditions employed for the NHPI-mediated process: $[(N4Py)Fe^{IV}=O]^{2+}$ (1.5 mM), X−NHPI (20 mol %) and triphenylmethane (30 mM). When compared with the background reaction, in the presence of all the X−NHPI mediators, a faster decay of $[(N4Py)Fe^{IV}=O]^{2+}$ at 690 nm was observed (Figures S9−S13 in the Supporting Information). From the data reported in Table 2, it can be noted that $t_{1/2}^0/$

Table 2. Decay Half-Life of the Iron(IV)−Oxo Complex $[(N4Py)Fe^{IV}=O]^{2+}$ ($t_{1/2}^0$) and Mediation Efficiency ($t_{1/2}^0/t_{1/2}^{med}$) in the Oxidation of Triphenylmethane Promoted by $[(N4Py)Fe^{IV}(O)]^{2+}$ (1.5 mM) in the Absence or in the Presence of X−NHPI Mediators in CH_3CN

mediator X−NHPI	$t_{1/2}^{med}$ (s)	mediation efficiency ($t_{1/2}^0/t_{1/2}^{med}$)
none	450	
4-NO$_2$	74	6.1
4-CO$_2$CH$_3$	43	10.5
3-F	31	14.5
H	33	13.6
4-CH$_3$	40	11.3
4-CH$_3$O	37	12.2

$t_{1/2}^{med}$ values are similar for all the X−NHPI mediators with the exclusion of 4-NO$_2$−NHPI for which the mediation efficiency is almost halved with respect to other mediators. In view of the more difficult oxidation of 4-NO$_2$−NHPI by the iron−oxo complex, the decrease of the mediation efficiency might indicate that the formation of 4-NO$_2$−PINO is kinetically relevant in the mediation process. With more easily oxidizable mediators, formation of the oxidized form of the mediator is very fast and the HAT process from the substrate to X−PINO likely plays a major role in the overall kinetic process.[31] Accordingly, a slight decrease in the mediation efficiency is found with 4-CH$_3$−PINO and 4-CH$_3$O−PINO, which are the least reactive N-oxyl radicals in HAT processes because of the unfavorable enthalpic and polar effects as reported in previous kinetic studies.[21,22,24,32]

The analysis of the time-resolved spectra for the oxidation of triphenylmethane (30 mM) with $[(N4Py)Fe^{IV}=O]^{2+}$ (1.5 mM) in the presence of 20 mol % of aryl-substituted NHPIs in the range of 380−1000 nm shows in all cases that the decay of $[(N4Py)Fe^{IV}=O]^{2+}$ is accompanied by the formation of the reduced iron complex $[(N4Py)Fe^{II}]^{2+}$ with its characteristic absorption maximum at 458 nm.[28] As an example, the time-resolved spectra recorded in the oxidation of triphenylmethane mediated by 4-NO$_2$−NHPI (time-resolved spectra for other mediators are reported in Figures S14−S18 in the Supporting Information) are reported in Figure 5. In this case as well as with all the mediators, the presence of an isosbestic point at 565 nm is clearly visible, which indicates that the first-formed reduced complex $[(N4Py)Fe^{III}−OH]^{2+}$ is very rapidly reduced to $[(N4Py)Fe^{II}]^{2+}$ by the triphenylmethyl radical produced after the HAT from X−PINO as reported in Scheme 5. Oxidation of the triphenylmethyl radical then leads to triphenylmethanol as revealed by product analysis (vide infra).

The dependence of the mediation efficiency on the substrate structure was tested using cyclohexane, toluene, and ethylbenzene. These substrates are characterized by C−H bond dissociation energies (BDEs) ranging from 81 kcal mol^{-1} (triphenylmethane) to 99.5 kcal mol^{-1} (cyclohexane)[33] (see Table 3) and second-order rate constants for the reaction with
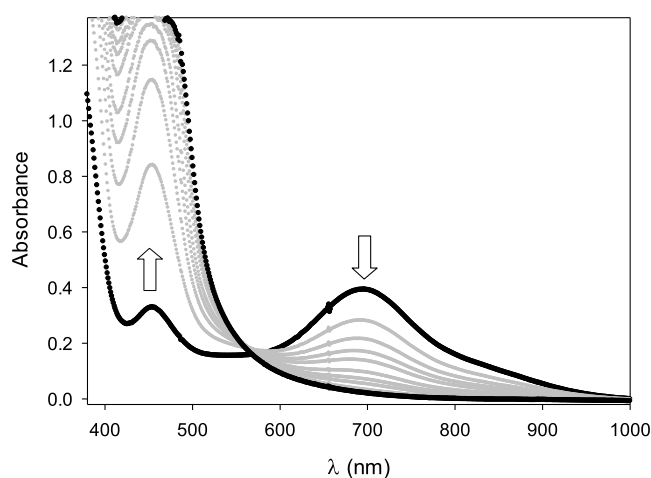

Figure 5. Time-resolved absorption spectra recorded in the oxidation of triphenylmethane (30 mM) with $[(N4Py)Fe^{IV}=O]^{2+}$ (1.5 mM) in the presence of 20 mol % of 4-NO$_2$−NHPI in CH_3CN.

$[(N4Py)Fe^{IV}=O]^{2+}$ spanning ca. 4 orders of magnitude from the least reactive cyclohexane ($k_H = 4.6 \times 10^{-6}$ M^{-1} s^{-1}) to the more reactive triphenylmethane ($k_H = 0.037$ M^{-1} s^{-1}).[11] The kinetic analysis was performed as described above for the reaction with triphenylmethane by adding the substrate (0.3−1.0 M) to a solution of $[(N4Py)Fe^{IV}=O]^{2+}$ (1.5 mM) and NHPI (20 mol %) in CH_3CN. With all the substrates, the decay of $[(N4Py)Fe^{IV}=O]^{2+}$ in the presence of NHPI was much faster than that recorded in the absence of a mediator (Figures S19−S21 in the Supporting Information). Analysis of the spectra taken at the end of the reaction indicated that the decay of $[(N4Py)Fe^{IV}=O]^{2+}$ is not accompanied by the quantitative formation of the reduced iron complex $[(N4Py)Fe^{II}]^{2+}$ as observed in the oxidation of triphenylmethane (Figures S22−S24 in the Supporting Information). As reported by Nam in the oxidation of ethylbenzene by $[(N4Py)Fe^{IV}=O]^{2+}$, complex $[(N4Py)Fe^{III}−OH]^{2+}$ is formed as the main reduced product accompanied by minor amounts of $[(N4Py)Fe^{II}]^{2+}$.[34] Probably, the benzylic radical formed after HAT from ethylbenzene, characterized by a higher redox potential with respect to the triphenylmethyl radical ($E_{1/2}^{ox} = 0.37$ and 0.21 V vs SCE in CH_3CN for PhCH$^\bullet$CH$_3$ and Ph$_3$C$^\bullet$, respectively[35]), is not oxidizable enough to reduce the iron(III)−hydroxo complex $[(N4Py)Fe^{III}−OH]^{2+}$ to $[(N4Py)Fe^{II}]^{2+}$.

From the values reported in Table 3, a significant variation of the mediation efficiency can be noted by changing the substrate with higher $t_{1/2}^0/t_{1/2}^{med}$ values observed with the least reactive substrates characterized by low C−H BDE values.

In order to confirm the mediation effect of NHPI in the oxidations promoted by $[(N4Py)Fe^{IV}=O]^{2+}$, we have carried out a product analysis study of the oxidation of triphenylmethane, ethylbenzene, and toluene with $[(N4Py)Fe^{IV}=O]^{2+}$ in the presence of NHPI (20 mol %) in CH_3CN under nitrogen (see details in the Experimental Section).

As reported in a previous study, oxidations of these substrates with $[(N4Py)Fe^{IV}=O]^{2+}$ in the absence of NHPI[11] lead to the formation of triphenylmethanol as the exclusive oxidation product of triphenylmethane, 1-phenylethanol, and acetophenone in the oxidation of ethylbenzene and benzaldehyde accompanied by minor amounts of benzyl alcohol in the oxidation of toluene. Products and yields referred to the amount of oxidant are reported in Table 4.[36]
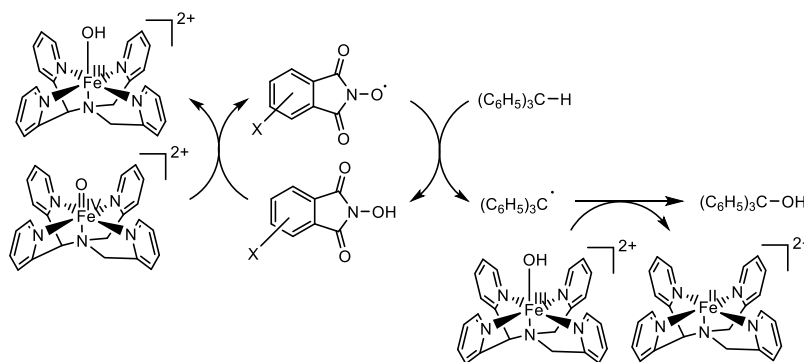
Scheme 5. Aryl-Substituted NHPIs Mediated Oxidation of Triphenylmethane Promoted by $[(N4Py)Fe^{IV}(O)]^{2+}$

Table 3. Decay Half-Life of the iron(IV)oxo Complex $[(N4Py)Fe^{IV}=O]^{2+}$ ($t_{1/2}^{med}$) and Mediation Efficiency ($t_{1/2}^{0}/t_{1/2}^{med}$) in the oxidation of Cyclohexane and Alkylaromatic Compounds Promoted by $[(N4Py)Fe^{IV}=O]^{2+}$ (1.5 mM) in the Absence or in the Presence of NHPI (20 mol %) in CH_3CN

substrate	C−H BDE kcal/mol[a]	$t_{1/2}^{0}$ (s)[b]	$t_{1/2}^{med}$ (s)	mediation efficiency ($t_{1/2}^{0}/t_{1/2}^{med}$)
cyclohexane[c]	99.5	32 000	990	32
toluene[d]	89.7	1680	52	32
ethylbenzene[e]	85.4	1080	40	27
triphenylmethane	81	450	33	13.6

[a]Ref 33. [b]Decay half-life in the absence of NHPI. [c][Cyclohexane] 0.8 M. [d][Toluene] 1 M. [e][Ethylbenzene] 0.3 M.

Table 4. Product Analysis in the oxidation of Alkylaromatic Compounds Promoted by $[(N4Py)Fe^{IV}=O]^{2+}$ in the Presence or Absence of 20 mol % NHPI as Mediator in CH_3CN^{a}

[a]$[(N4Py)Fe^{IV}=O]^{2+}$ (19 mM) and substrate (190 mM) in CH_3CN (1 mL). Yields (mol %) refer to the amount of oxidant and have been determined by GC. [b]Reaction time 1 h. [c]Reaction time 30 min. [d]Reaction time 1 min.

The results of product analysis clearly indicate that with all the substrates tested, significant higher yields of products are observed in the presence of the NHPI mediator when reaction times were limited to 1, 30, and 60 min for triphenylmethane, ethylbenzene, and toluene, respectively. Thus, product analysis confirms the results of kinetic studies, indicating a faster and more efficient oxidation of hydrocarbons by $[(N4Py)Fe^{IV}(O)]^{2+}$ in the presence of the NHPI mediator.

Product analysis of the oxidation of triphenylmethane has been also carried out under catalytic conditions in iron-catalyst $[(N4Py)Fe^{II}]^{2+}$ using peroxyacetic acid as the oxidant. The use of PhIO was not possible as it oxidizes directly also the NHPI mediator. To a solution of $[(N4Py)Fe^{II}]^{2+}$ (8 μmol in CH_3CN), NHPI (2 μmol) and triphenylmethane (0.1 mmol) in 1 mL CH_3CN, 10 μL of the oxidant CH_3COOOH (40% w/w in AcOH, 61 μmol) was added and the mixture was stirred at 25 °C for 5 min. Even under catalytic conditions, the mediated process was more efficient, with the amount of triphenylmethanol produced in the presence of NHPI (23 μmol, 38% refers to the amount of oxidant) being much higher than that observed in the absence of NHPI (12 μmol, 20% refers to the amount of oxidant).

■ CONCLUSIONS

NHPI is able to efficiently mediate the oxidation of hydrocarbons promoted by the nonheme iron(IV)−oxo complex, $[(N4Py)Fe^{IV}(O)]^{2+}$. The increase of reactivity is associated to the oxidation of the mediator to the phthalimide N-oxyl radical (PINO), which in turn efficiently abstracts a hydrogen atom from the substrates regenerating the mediator in its reduced form.

The reactivity enhancement induced by the N-hydroxy mediators may be useful especially with iron(IV)−oxo complexes characterized by an intrinsic low reactivity. The analysis of the dependence of the mediation efficiency on the ligand structures of the iron(IV)−oxo complexes is currently underway in our laboratory. Finally, it has to be added that the presence of redox mediators may determine a variation of the HAT selectivity displayed by the iron(IV)−oxo complexes. Using suitable probe substrates containing different C−H bonds, it will be possible to investigate the effect of N-hydroxy mediators on the reaction selectivity by comparing the results of product analysis carried out in the absence and in the presence of mediators.

■ EXPERIMENTAL SECTION

Materials. CH_3CN (spectrophotometric grade), NHPI, were used as received. Aryl-substituted NHPIs (X−NHPI, X = 4-NO$_2$, 4-

CO_2CH_3, 3-F, 4-CH$_3$, 4-OCH$_3$) were synthetized according to the literature.[21,25] Iodosylbenzene was prepared by a literature method and stored at −20 °C under inert atmosphere.[37] [(N4Py)Fe(OTf)$_2$] was prepared by metalation of the ligand N4Py with Fe(OTf)$_2$ according to a literature method.[29] [(N4Py)Fe^{IV}=O] was prepared by reacting [(N4Py)Fe(OTf)$_2$] with excess solid PhIO.[11]

Spectrophotometric Analysis of the Reaction of [(N4Py)-Fe^{IV}=O]$^{2+}$ with X−NHPI Mediators. Spectroscopic analysis was performed on a single beam UV−vis spectrophotometer using a quartz cuvette (10 mm path length) at 25 °C. A solution of [(N4Py)Fe^{IV}=O]$^{2+}$ (1.5 mM in CH$_3$CN) was prepared by oxidation of the corresponding iron(II) complex [(N4Py)Fe^{II}(OTf)$_2$] with a slight excess of solid PhIO (1.2 equiv). After 30 min, the solution was filtered and a 20 mol % of X−NHPI (X = H, 3-F, 4-CH$_3$, 4-OCH$_3$) with respect to [(N4Py)Fe^{IV}=O]$^{2+}$ was added.

Kinetic Studies of the Oxidation of Triphenylmethane by [(N4Py)Fe^{IV}=O]$^{2+}$ in the Presence of X−NHPI Mediators. Spectrophotometric measurements were performed on a single beam UV−vis spectrophotometer using a quartz cuvette (10 mm path length) at 25 °C. A solution of [(N4Py)Fe^{IV}=O]$^{2+}$ (1.5 mM in CH$_3$CN) was prepared by oxidation of the corresponding iron(II) complex [(N4Py)Fe^{II}(OTf)$_2$] with a slight excess of solid PhIO (1.2 equiv). After 30 min, the solution was filtered and NHPI (5−25 mol % with respect to [(N4Py)Fe^{IV}=O]$^{2+}$) was added followed by the solution of triphenylmethane (30 mM). Time-resolved spectra were then recorded in the 380−1000 nm range.

Rates of substrate oxidation were monitored following the decay of the [(N4Py)Fe^{IV}=O]$^{2+}$ at 690 nm.[11] In a blank experiment, the oxidation of triphenylmethane 30 mM promoted by [(N4Py)Fe^{IV}=O]$^{2+}$ was carried out in the absence of the mediator under the same reaction conditions described above.

Kinetic Studies of the Oxidation of Cyclohexane and Alkylaromatic Compounds by [(N4Py)Fe^{IV}=O]$^{2+}$ in the Presence of NHPI. A solution of [(N4Py)Fe^{IV}=O]$^{2+}$ (1.5 mM in CH$_3$CN) was prepared as above. After 30 min, the solution was filtered and NHPI (20% with respect to [(N4Py)Fe^{IV}=O]$^{2+}$ was added followed by a solution of substrate (0.3−1 M). The rates of substrate oxidation were monitored following the decay of the [(N4Py)Fe^{IV}=O]$^{2+}$ (absorption band at 690 nm). In blank experiments, the oxidations of substrates promoted only by [(N4Py)Fe^{IV}=O]$^{2+}$ were performed in the same conditions described above.

Product Analysis of the Oxidation of Alkylaromatic Compounds with [(N4Py)Fe^{IV}=O]$^{2+}$ in the Absence and in the Presence of NHPI. A solution of [(N4Py)Fe^{IV}=O]$^{2+}$ (19 mM in CH$_3$CN) was prepared by oxidation of the corresponding iron(II) complex [(N4Py)Fe^{II}(OTf)$_2$] with a slight excess of solid PhIO (1.2 equiv). After 30 min, the solution was filtered and NHPI (20% with respect to [(N4Py)Fe^{IV}=O]$^{2+}$) was added followed by a solution of the substrate (190 mM). The mixture was vigorously stirred at 25 °C for 60, 30, or 1 min for toluene, ethylbenzene, and triphenylmethane, respectively, under nitrogen or air. Then, an internal standard was added (nitrobenzene, 10% with respect to the substrate), the reaction mixture was filtered over a short pad of SiO$_2$ with AcOEt, and analyzed by gas chromatography (GC) and gas chromatography−mass spectrometry (GC−MS). Blank experiments were carried out in the absence of the mediator in the same conditions.

Product Analysis of the Oxidation of Triphenylmethane with Peracetic Acid Catalyzed by [(N4Py)Fe^{II}]$^{2+}$ in the Absence and in the Presence of NHPI. To a 1 mL stirred solution of [(N4Py)Fe^{II}]$^{2+}$ (8 mM in CH$_3$CN), NHPI (2 mM) and triphenylmethane (0.1 M) in CH$_3$CN at 25 °C, 10 μL of the oxidant CH$_3$COOOH (40% w/w in AcOH, 61 μmol) was added in five portions of 2 μL every minute (total reaction time 5 min). Then, an internal standard was added (nitrobenzene, 10% with respect to the substrate), the reaction mixture was filtered over a short pad of SiO$_2$ with AcOEt, and analyzed by GC and GC−MS. Blank experiments were carried out in the absence of the mediator in the same conditions.

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Notes
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