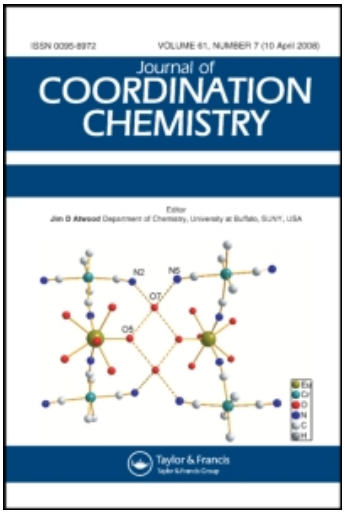

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The Fe-catalyzed oxidation of aroyl hydrazones to aroyl hydrazines: mechanistic insight to a remarkable reaction

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The Fe-catalyzed oxidation of aroyl hydrazones to aroyl hydrazines: mechanistic insight to a remarkable reaction

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The Fe^{III}-catalyzed oxidation of pyridinecarbaldehyde isonicotinoyl hydrazone to isonicotinoyl picolinoyl hydrazine in aqueous solution has been studied from a kinetico-mechanistic perspective. The reaction is more complex than one would anticipate from the known simple and reproducible preparative procedures. A series of very fast ligand coordination reactions to the Fe^{III} center are followed by slower –N=CH– bond hydrolysis and rapid ligand-to-metal electron transfer coupled to $H^{\bullet}$ elimination. These processes lead to a partially oxidized ligand mixture with Fe^{II} coordinated to unreacted hydrazone. The slow decomposition of this Fe^{II}-hydrazone complex in aerobic alkaline solution produces ferric hydroxide as a new source of Fe^{III} to sustain the hydrazone (–CO–NH–N=CH–) to hydrazine (CO–NH–NH–CO–) oxidation.

Keywords: Iron chelators; Mechanism; Hydrazone oxidation

1. Introduction

Aroyl hydrazones and hydrazines are related but distinctly different compounds that are essentially non-interconvertible by conventional organic chemistry. Sometime ago, we reported the facile conversion of pyridinecarbaldehyde isonicotinoyl hydrazone (HPCIH) to isonicotinoyl picolinoyl hydrazine (H_2IPH) catalyzed by iron(III) in mildly acidic aqueous solution resulting in [Fe^{III}(IPH)(HPIH)] as the unexpected product (scheme 1) [1]. Similar chemistry was identified when the corresponding pyridinecarbaldehyde picolinoyl hydrazone (HPCPH) was reacted with Fe(III) although the product was a most unusual dinuclear, mixed hydrazone–hydrazine triple helicate [2].

Both the HPCIH and H_2IPH series are tridentate *N*,*N*,*O* chelators, yet their coordination chemistry is very different. The HPCIH analogs are highly selective toward Fe^{II} [3], and we have been able to isolate a stable and pure Fe^{II} complex from this series. During one particular attempt at Fe^{III} complex formation, we were surprised to find that the HPCIH ligand converted into H_2IPH (scheme 1) [1]. Fortunately, both

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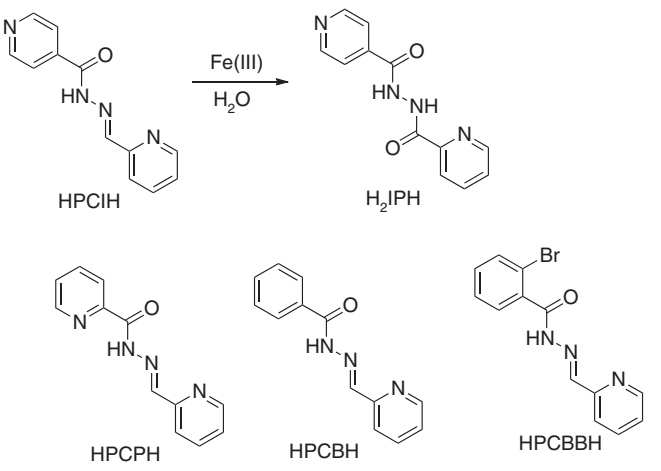


Scheme 1. Solution reactivity and hydrazone ligands refered to in this study.

the HPCIH [3, 4] and H_2IPH [1, 5] analogs are active Fe chelators and show great promise as novel drug candidates in the treatment of Fe overload disorders [6].

These reactions may be formally considered as two-electron hydroxylation reactions of the imine carbon (followed by tautomerism from the enol) to give the stable hydrazine (scheme 1) but the actual mechanistic details are almost certainly not so simple. A report about the problematics about iron/ligand oxidation states in catalytic processes has appeared very recently [7]. There are parallels in the literature with imine (Schiff base) chemistry in the presence of Ru and Re where the corresponding amides have been formed [8–11]. The mechanism by which the hydrazone to hydrazine reaction of the iron complexes occurs and the involvement of iron in complexation with the starting material and possible intermediates, especially under preparative conditions, has remained unclear until now [3].

With all these observations in mind, we have studied this solution reactivity to understand the mechanism of these processes observed under preparative conditions. The decomposition of $[Fe^{II}(PCIH)_2]$ under controlled alkaline conditions and reactions of Fe^{II} with H_2IPH and Fe^{III} with HPCIH in alkaline medium and pure acetonitrile have been studied.

2. Experimental

2.1. *Compounds*

HPCIH and H_2IPH ligands as well as the corresponding $[Fe^{II}(PCIH)_2]$ and $[Fe^{III}(IPH)(HIPH)]$ complexes have been prepared according to the methods described in literature [1, 12]. All other chemicals were reagent grade from Aldrich and used as received.

2.2. *Kinetics*

All reactions were monitored by UV-Vis spectroscopy from 800 to 300 nm. Observed rate constants were derived from the absorbance *versus* time traces at wavelengths where a maximum increase and/or decrease of absorbance was observed without interference from other absorbing species [13]. The general kinetic technique is that previously described [14–16]. The observed rate constants were determined by analyses performed with Specfit [17]. Kinetic runs were recorded on a Cary50 or a HP8452A instrument, equipped with a thermostated multicell transport, or on an Applied Photophysics stopped-flow mixing unit connected to a TIDAS instrument.

3. Results and discussion

3.1. *Reactivity of [Fe^{II}(PCIH)$_2$] in alkaline conditions*

The [Fe^{II}(PCIH)$_2$] complex has been fully characterized and its stability in non-aqueous solvents established [4, 18]. Nevertheless, on a preparative scale, the reaction between Fe^{III} and HPCIH with the intention of producing $[Fe^{III}(PCIH)_2]^+$ yields [Fe^{III}(IPH)(HIPH)] instead, although the reaction mixture contains other uncharacterized species [1]. As a starting point, the stability and reactivity of the [Fe^{II}(PCIH)$_2$] complex in aqueous solution at varying pH is of key importance. This has been investigated here at buffered ($I = 0.1\ mol\ L^{-1}$) pH values between 7.7 and 9.5, where the 1 : 2 Fe^{II} : ligand complex is known to be formed completely; at lower pH, partial dissociation of the Fe^{II} complex occurs [3]. Reactions were initiated by the addition of an MeCN solution of [Fe^{II}(PCIH)$_2$] (poorly soluble in water alone) to a buffered thermostated aqueous solution. The final MeCN concentration was no more than 2% (v/v), but this was sufficient to maintain its solubility in the predominantly aqueous solution.

Under these conditions with N_2 purged solutions no reactivity is observed, indicating that the initial *bis*-hydrazone complex is completely stable at these pH values in the absence of air. For aerated solutions, the characteristic absorption maximum at 630 nm (due to Fe^{II}-to ligand charge transfer) vanishes and the peak at 340 nm (ligand-to-ligand charge transfer for the Fe^{II} complex) shifts to 305 nm (corresponding to the peak observed for the free HPCIH ligand at these pH values, figure S1). Figure 1(a) indicates the changes observed in the time-resolved monitoring of the electronic spectrum.

The electronic spectrum of the final reaction mixture lacks peaks corresponding to either the well-characterized [Fe^{III}(IPH)(HIPH)] complex or H_2IPH free ligand at this pH (figure S1) [5]. The process observed corresponds to a simple dissociation of the Fe^{II} complex with no ligand oxidation under these conditions. The participation of oxygen in the reaction clearly points to irreversible oxidation of ferrous ions in basic solution coupled to the observation of a finely dispersed brown precipitate. Given the intensity of the MLCT band in the spectrum of [Fe^{II}(PCIH)$_2$], such an interference is only detected as a very small shift on the absorbance on the final spectrum that does not affect, within error, the value of k_{obs}. The formation of insoluble ferric hydroxide is the driving force for this irreversible process. The initial [Fe^{II}(PCIH)$_2$] complex although apparently stable under these pH conditions in the absence of air is clearly in equilibrium with a minute amount of partially dissociated complex. In the presence

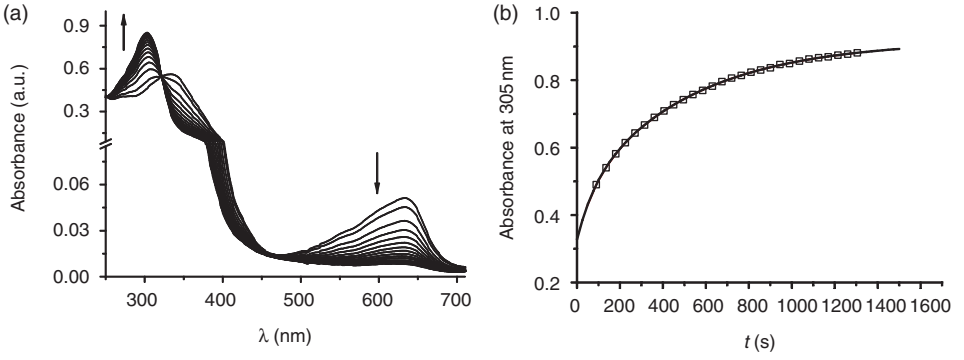


Figure 1. (a) Changes in the electronic spectrum of a sample of $[Fe^{II}(PCIH)_2]$ dissolved in oxygenated borax buffer at pH 8.4. (b) Absorbance *vs.* time trace for the same experiment with the solid line showing the fit to a biexponential process.

of air, oxidation of the partially dissociated Fe^{II} complex is irreversible leading ultimately to complete conversion to ferric hydroxide and HPCIH free ligand.

Absorbance *versus* time traces obtained from the time resolved spectra indicated in figure 1(b) have a definite biphasic character and can be very well fitted to a set of two consecutive processes [17], both of which are pH dependent (figure 2). The exact nature of the two processes is not clear, but probably relates to a sequential substitution of coordinated $PCIH^-$ by OH^- preceding oxidation and precipitation of ferric hydroxide. The same general profile process has been observed for other hydrazone ligands of the same family without the isonicotinoyl moiety (HPCBH, HPC2BBH, scheme 1) [3].

Further analysis was carried out on complex hydrolysis equilibria involving the Fe : PCIH system in different solvents. Figure 3(a) shows a plot for different solvents of the energy of the MLCT band in the 650 nm region *versus* $(1/D_{op}-1/D_S)$, D_{op} and D_S being the optical and static dielectric constants of the solvent [17, 19]. From the plot, it is evident that the shift observed in the maximum does not correspond with the expected linear trend [19], indicating that $[Fe^{II}(PCIH)_2]$ coexists with other partially solvated forms. Furthermore, dilution of the samples does not follow the Beer–Lambert law which is indicative of concentration dependent solvolysis equilibria (figure 3b) [20].

3.2. *Reactivity of the Fe^{III}/HPCIH system in aqueous solution*

It is apparent from the previous section that Fe^{II} complexes of the HPCIH analogs are not precursors of the hydrazone to hydrazine transformation; the only reactivity they show is complex dissociation in oxygenated alkaline solution. In view of this, the direct reaction of Fe^{III} with HPCIH was monitored in water in mildly acidic buffers (pH 3.5–4.5; $I = 0.1\ mol\ L^{-1}$), and under stoichiometric conditions (Fe : HPCIH = 1 : 2) with UV-Vis spectroscopy.

Below pH 2.5, no reaction is observed due to protonation of the ligand which prevents complex formation, while above pH 4.5, a brown precipitate characteristic of ferric hydroxide is formed before complex formation [20]. The reaction within the 3.5–4.5 pH range shows very complex spectral changes (figure 4), and the spectrum of the final equilibrated sample does not correspond with that described for

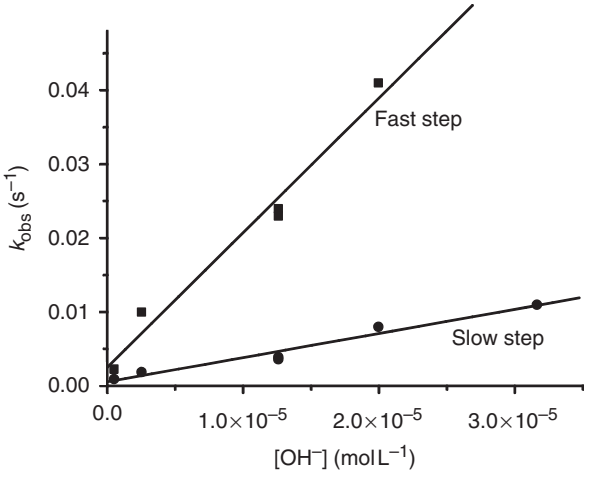


Figure 2. Plots of the observed rate constants *vs.* [OH^-] for decomposition of [$Fe^{II}(PCIH)_2$] at 25°C and $I = 0.1\,mol\,L^{-1}$ (Borax aerated buffer).

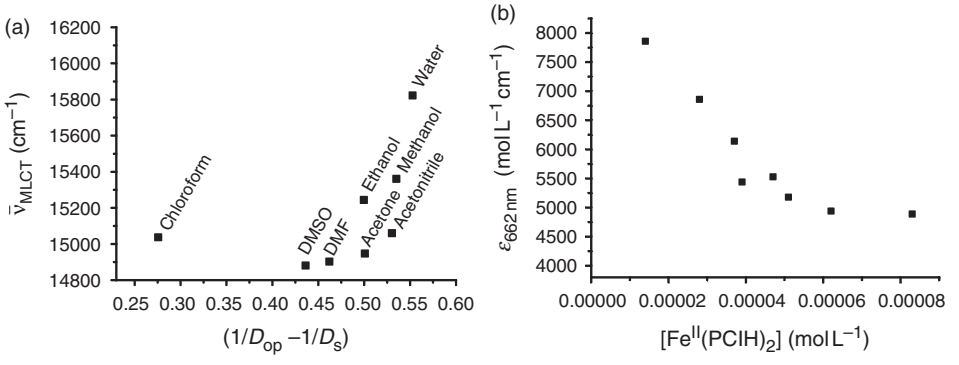


Figure 3. (a) Plot of the MLCT band energy *vs.* the $(1/D_{op} - 1/D_S)$ for different solvents of a solution of [$Fe^{II}(PCIH)_2$]. (b) Changes of the apparent extinction coefficient of the MLCT band at 662 nm of a solution of [$Fe^{II}(PCIH)_2$] in acetonitrile.

[$Fe^{III}(IPH)(HIPH)$] alone (figure S1) [5]. Furthermore, when the pH is increased to 7.5, the appearance of [$Fe^{II}(PCIH)_2$] is immediately evident [3, 12]. All these processes occur independent of the presence of oxygen. The appearance of bubbles during the reaction is germane.

It is thus clear that during the reaction the initially 100% starting Fe^{III} solution is at least partially reduced to Fe^{II} (coupled with HPCIH to ligand oxidation) as it is recaptured by excess HPCIH in solution upon neutralization to generate [$Fe^{II}(PCIH)_2$] as a dead-end species. The fact that no [$Fe^{III}(IPH)(HIPH)$] is detected under these carefully controlled conditions (and at higher dilution than under preparative scales) may be due to unfavorable stoichiometry. In the absence of an external oxidant, such as dioxygen, at least a 5:1 ([Fe^{III}]:[HPCIH]) concentration ratio is needed for the theoretical redox reaction (HPCIH to H_2IPH) to occur quantitatively (four Fe^{III} ions

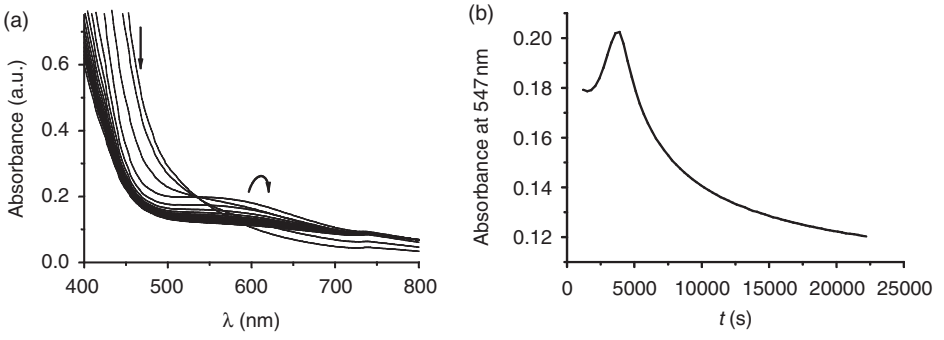


Figure 4. (a) Changes in the electronic spectrum of the reaction of Fe^{III} with HPCIH in a 1:2 stoichiometry at pH 3.8. (b) Absorbance *vs.* time profiles for the same experiment at 547 nm (acetate buffer $I = 0.1\,mol\,L^{-1}$, $[Fe] = 7.5 \times 10^{-4}\,mol\,L^{-1}$).

accepting a total of four electrons from the two ligands and the remaining Fe^{III} complexing the two oxidized ligands).

Oxygen-free experiments involving stoichiometric concentrations of Fe^{II} and the preformed hydrazine H_2IPH ligand at pH values between four and eight indicate that no Fe^{III} complex formation occurs appreciably in water in the absence of an oxidant. The reaction does proceed when air is admitted leading to the stable $[Fe^{III}(IPH)(HIPH)]$ complex. Similarly, experiments run on degassed MeCN solutions of $FeCl_2$ and H_2IPH/NEt_3 show no reaction until air is admitted to the mixture. It is apparent that H_2IPH has a low affinity for Fe^{II}.

The extremely complex absorbance *versus* time profiles for the Fe^{III}/HPCIH reaction (figure 4b) only allow for semi-quantitative interpretations. For the fast reaction steps (*ca* 1 h at room temperature), a significant acceleration is observed with increasing ligand concentration, thus indicating that ligand coordination is relevant [21]. The rates also become faster at lower pH, perhaps counterintuitive considering the ligand concentration dependence [22]. The fact that the overall process requires both the coordination of the HPCIH ligand to Fe^{III} and the subsequent dissociation of a modified ligand from Fe^{II} (IPH^{2-} or $HIPH^{-}$) explains this apparent discrepancy. As for the slow step observed in these profiles, its rate is essentially independent of both the ligand concentration and the amount of acid which implies an intramolecular process.

A significant observation is the appearance of gas bubbles during the reaction between Fe^{III} and HPCIH. Experiments were conducted under conditions where the evolved gas was collected in an evacuated and cooled Schlenk tube from where it was clear that no O_2 was evolving from the reaction (as determined with a CRISON oxymeter OXI330 detector with a sensor cell OX305); H_2 is then the only remaining gaseous product that can be formed.

3.3. *Reactivity of the Fe^{III}/HPCIH system in MeCN*

The reaction of anhydrous $FeCl_3$ with HPCIH in neat MeCN was monitored in the presence of variable amounts of Et_3N and water. The mixing of HPCIH and $FeCl_3$

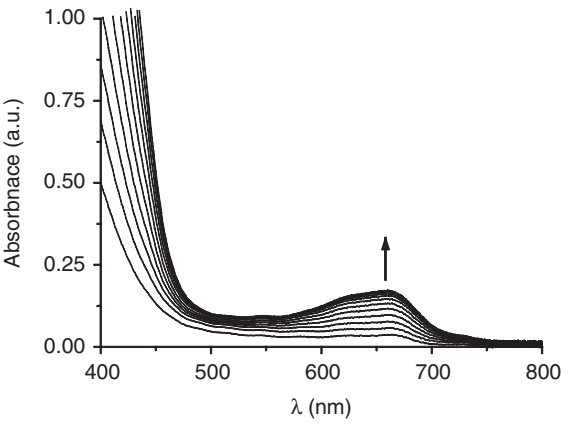


Figure 5. UV-Vis spectral changes for the reaction of Fe^{III}, HPCIH and NEt_3 in 100% MeCN ($[Fe^{III}] = 7.5 \times 10^{-5}$ mol L^{-1}; $[HPCIH] = 8 \times 10^{-4}$ mol L^{-1}; $[NEt_3] = 8 \times 10^{-3}$ mol L^{-1}; 35°C) final reaction time 60 min.

in MeCN at different concentration ratios does not produce any measurable reactivity on the manual mixing timescale. Nevertheless, initially a stable ferric complex in a protonated form is apparently formed with an electronic spectrum different from that of the starting materials. Addition of a twofold molar ratio of Et_3N to these solutions produces a UV-Vis spectrum with a broad maximum in the 600–500 nm region, indicative of the Fe^{III} complex from these types of ligands (figure S1) [5]. The X-band EPR spectrum of a frozen solution of this product (77 K) is characteristic of an axially symmetric low-spin Fe^{III} complex as reported; the same result is obtained with an electrochemically oxidized solution of $[Fe^{II}(PCIH)_2]$ in MeCN [2].

The process is independent of the relative concentrations of $FeCl_3$, HPCIH ligand, or added Et_3N and, on standing, these ferric solutions slowly develop an intense green color characteristic of $[Fe^{II}(PCIH)_2]$ within 1–2 h at 35°C (figure 5). The Fe^{III} complex is clearly a very strong oxidant and is able to oxidize any nucleophilic species in solution e.g., chloride, Et_3N, MeCN, or traces of water on returning to its stable Fe^{II} form. No reliable kinetic data could be obtained for the time dependence of the spectra. Addition of water to these solutions up to concentrations of 0.25 mol L^{-1} does not produce any significant changes; higher concentrations of water produced a brown precipitate of ferric hydroxide without formation of $[Fe^{II}(PCIH)_2]$. Results indicate that the changes observed after manual mixing do not correspond to oxidation reactions of the coordinated ligands, but are merely subsequent ligand exchange reactions triggered by ligand dissociation.

In order to quantify the $Fe^{II}/PCIH^-$ and Fe^{III}/IPH^{2-} complexation processes, stopped-flow experiments on mixtures of $FeCl_2/PCIH^-$ and $FeCl_3/IPH^{2-}$ in MeCN were conducted in 1 : 20 and 1 : 6 concentration ratios, respectively, in the $(2–5) \times 10^{-4}$ mol L^{-1} concentration range (the low solubility of $FeCl_2$ and IPH^{2-} did not allow a wider range). Under these conditions, the $FeCl_2/PCIH^-$ mixture reacts within the mixing time of the instrument to give a typical spectrum of $[Fe^{II}(PCIH)_2]$ (figure S1), while that of $FeCl_3/IPH^{2-}$ shows two consecutive processes (on timescales

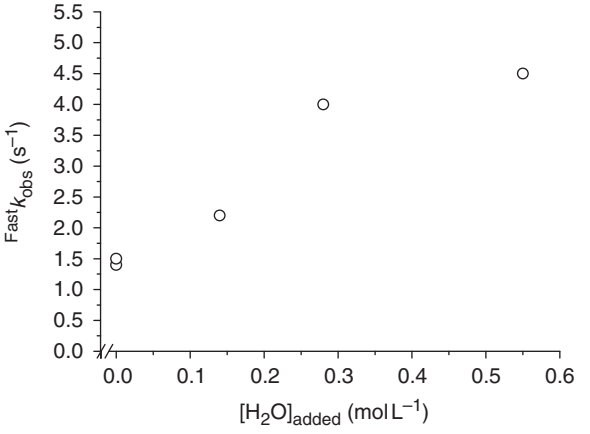
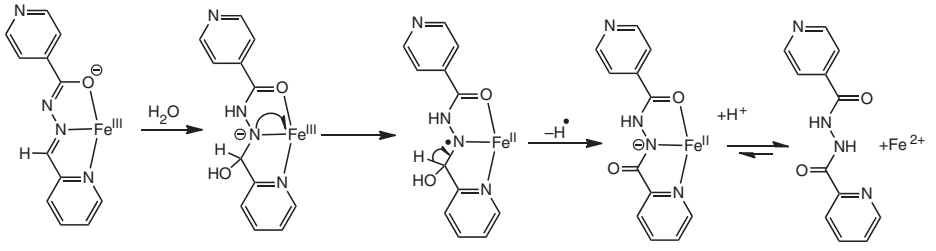


Figure 6. Plot of the changes of the observed rate constant for the faster reaction monitored from stopped-flow mixing of Fe^{III} and $PCIH^-$ in MeCN (as purchased) with different concentrations of water added ($[HPCIH] = 8 \times 10^{-4}\,mol\,L^{-1}$; $[NEt_3] = 8 \times 10^{-3}\,mol\,L^{-1}$; $[Fe^{III}] = 7.5 \times 10^{-5}\,mol\,L^{-1}$; 25°C).

of *ca* 6 and 15 s) which produce a UV-Vis spectrum with a broad maximum at 560 nm, typical for the Fe^{III} complexes of the IPH^{2-} hydrazine ligands in MeCN [5]. The difference is consistent with the four order of magnitude increase for the rate constants of the water exchange processes occurring at Fe^{III} and Fe^{II} [23].

The reaction of $FeCl_3$ with $HPCIH/Et_3N$ on the stopped-flow timescale was consequently studied at various MeCN/water mixtures. For commercial "dry" MeCN, the observed reaction involves a set of two consecutive processes on the 6 and 30 s time scales, neither being dependent on ligand or metal concentrations. Nevertheless, an increase in water content produces a definite acceleration of the faster process (figure 6); for $[H_2O] > 0.5\,mol\,L^{-1}$ the spectral changes become too fast to be observed relative to the mixing time of the instrument.

From available data, we propose the initial formation of a $Fe^{III}/PCIH^-$ complex on a similar time scale to the Fe^{III}/IPH^{2-} reaction. Rapid C=N bond hydrolysis (scheme 2, first step) occurs, and this is naturally dependent on water concentration. Given the fact that concentration of the iron complexes is around $10^{-4}\,mol\,L^{-1}$ in our experiments, there will inevitably be at least a stoichiometric amount of water present even in commercial "dry" MeCN for an 1 : 1 nucleophilic attack by water on each C=N bond without any additional water added (figure 6). We assume that the internal ligand to Fe^{III} electron transfer (scheme 2, step 2) that follows should take place rapidly [8–11] and cannot be related with the changes observed. Decomposition of the putative $\{Fe^{II}/(IPH)\}$ units, formed after ligand oxidation, in the absence of air should thus be responsible for the slow changes observed in the spectra on manual mixing. After decomposition, the ferrous hydrazine complex, the more stable green $[Fe^{II}(PCIH)_2]$ complex is formed through the capture of the free ferrous ions by excess hydrazone [3]. We have shown that this complex is unstable at high pH in the presence of oxygen (section 3.1), the driving force for the decomposition being the production of ferric hydroxide. Alternatively, air oxidation of solutions containing Fe^{II} and H_2IPH should lead to the preparatively obtained $[Fe^{III}(IPH)(HIPH)]$ complex.



Scheme 2. Mechanism proposed for the observed reaction sequence in this work.

4. Conclusions

The mechanism summarized in scheme 2 accounts for the processes we have been able to observe and also includes steps too fast to see, but inferred from the products we have identified. Coordination of HPCIH to Fe^{III} generates a highly reactive ferric species, where the ligand is activated for water nucleophilic attack [22, 13] and also where the complex formed is highly oxidizing from the known high $Fe^{III/II}$ redox potential of $[Fe(PCIH)_2]^{+/0}$ [3]. These putative and highly reactive $\{Fe^{III}/(PCIH)\}$ units undergo oxidation of the ligand after C=N bond hydration with consequent reduction of the metal. Dissociation of the ensuing H_2IPH hydrazine from Fe^{II} is then spontaneous at mildly acidic pH. Ultimately, the H_2IPH recoordinates to Fe^{II} (or Fe^{III}) and in the presence of oxygen a stable $[Fe^{III}(IPH)(HIPH)]$ complex is formed as one of the many products. Unreacted HPCIH is captured by Fe^{II} generating $[Fe^{II}(PCIH)_2]$ as another major species.

In the absence of oxygen, $[Fe^{II}(PCIH)_2]$ is stable and formed rapidly when free ferrous ions are reacted with HPCIH at neutral pH. This is an important issue in the potential application of HPCIH and its analogs as a chelator for the treatment of Fe overload disorders [6]. The results we have presented may have even more significance in highlighting the conditions under which the Fe-catalyzed oxidation of HPCIH to H_2IPH might occur in a biological context. Both sets of ligands are very effective in mobilizing Fe from cells [1, 3, 5], and it is possible that similar chemistry occurs in the cell if HPCIH encounters Fe^{III}. On the basis of this study and others in the past, we can be sure that the ferric complex $[Fe(PCIH)_2]^+$ has no biological significance. It is highly reactive and can only be observed in non-aqueous solution (MeCN) for a limited time. The pyridyl and imine N-donors strongly favor the ferrous form of their Fe complexes. The H_2IPH hydrazine ligand is distinctly different, in fact opposite, to the hydrazones in its preference for Fe^{III} and instability of its Fe^{II} complexes has emerged from this study as a key feature in the overall mechanism.

Comparison with already published similar imine to amide oxidation reactions occurring on rhenium and ruthenium centers [10, 11] in high oxidation states raises an important issue on the evolution of gas bubbles during the process as a mechanistic determinant. While for the Re^{IV} or Ru^{III} centers the initial step is considered an H radical extraction by an external metal center in a high oxidation state followed by an internal electron transfer from the ligand to the metal center [9]; in our present case we propose an initial internal $1e^-$ redox process followed by hydrogen atom elimination (and dimerization producing dihydrogen) without the acquiescence of an external Fe^{III} ion.

Acknowledgments

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