# Mechanistic Studies on the Oxidation of Nitrite by a $\mu$-Oxodiiron(III,III) Complex in Aqueous Acidic Media

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Examined in this study is the kinetics of a net $2e^-$ transfer between $[Fe_2(\mu\text{-}O)(phen)_4(H_2O)_2]^{4+}$ (**1**) and its hydrolytic derivatives $[Fe_2(\mu\text{-}O)(phen)_4(H_2O)(OH)]^{3+}$ (**2**) and $[Fe_2(\mu\text{-}O)(phen)_4(OH)_2]^{2+}$ (**3**) with $NO_2^-$ in aqueous media and in presence of excess 1,10-phenanthroline (phen). The reaction is quantitative with a 1:1 stoichiometry between the oxidant and reductant to produce ferroin ($[Fe(phen)_3]^{2+}$) and $NO_3^-$. The order of reactivity of the oxidant species is **1** > **2** > **3**, in agreement with the progressive cationic charge reduction. The reactions appear to be inner-sphere where the initial one-electron proton-coupled redox ($1e^-$, $1H^+$; electroprotic) seems to be rate-determining.

**Introduction.** – Proteins containing nonheme, nonsulfur, carboxylato- or oxo-bridged diiron sites have not escaped the apparently irresistible tendency of chemists and biochemists to classify natural phenomenon (quoted from [1]). Most of these proteins react with dioxygen as a part of their functional processes, which are perhaps the mostly studied among many of their biological processes. Among these studies, exploration of the structures of several diiron(II) sites and insights into the high-valent oxodiiron intermediates are included. Synthetic chemistry has already suggested many novel structures that are structural and sometimes also functional models for these high-valent iron species as well as for diiron(II) sites [2].

However, reactivity studies of these model di- or polyiron species appear to be occasional [3], and mechanistic studies are extremely rare [4] outside a protein environment, whereas quite a lot of reactivity and kinetic studies on addition reactions to iron centers and subsequent redox changes of diiron sites in ribonucleotide reductase (RNR) [5], hemerythrin (Hr), semimetHr and metHr [6] with a broad spectrum of small ligands as well as reducing agents are known. The lack of information on reactivity of model oxodi- or oxopolyiron complexes is possibly due to the high stability of the $\mu$-oxodiiron(III,III) unit that translates to inertness under a variety of conditions and is, in fact, one likely reason for the availability of quite a large number of synthetic complexes with the Fe–O–Fe unit.

The complex salt $[Fe_2(\mu\text{-}O)(phen)_4(H_2O)_2](NO_3)_4 \cdot 5H_2O$ (phen = 1,10-phenanthroline; **1**; *Fig. 1*) selected for the present investigation, is an attractive *Raman*-spectroscopy model for the binuclear iron site in the RNR and metHr, the oxidized form of the oxygen-transport protein hemerythrin [7]. Its conjugate base, $[Fe_2(\mu\text{-}O)(phen)_4(H_2O)(OH)]^{3+}$ (**2**) is also a possible functional model for the purple acid phosphatase [2a][8]. The dinuclear complex **1** is soluble in $H_2O$, and the solution is fairly stable towards self-decomposition in a wide pH range (3.0–7.0) in presence of added 1,10-

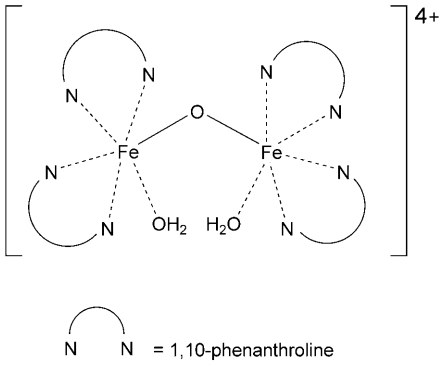


Fig. 1. *Structure of* $[Fe_2(\mu\text{-}O)(phen)_4(H_2O)_2]^{4+}$

phenanthroline. The $\mu$-oxo bridges in such complexes are potential proton-acceptor sites that allow electron transfer coupled with proton movements from reducing substrates or solvent to the oxo bridges, and this lowers the activation barrier for thermodynamically unfavorable reactions [3b]. Reversible oxygenation to deoxyhemerythrin, disproportionation/reduction of mixed-valent forms of diiron sites in hemerythrin [9], reaction of NO [6d,e], $HNO_2$ [6b], or $H_2O_2$ [6a,c] with deoxyhemerythrin unambiguously demonstrate that the oxo-bridge protonation is an essential prerequisite for the above-mentioned redox processes. Recently, we observed that complex **1** and its hydrolytic derivatives are reduced by $N_2H_4$ by the very similar proton-coupled electron-transfer (PCET) pathways [4f].

We now find that complex **1** oxidizes nitrite and the reaction rate is considerably lowered in $D_2O$, again suggesting simultaneous $e^-$ and $H^+$ transfer in the rate-limiting step of the redox reaction of **1** and nitrite. We like to note here that nitrite, in the form of $HNO_2$, oxidizes deoxyHr ($Fe^{II}$,$Fe^{II}$) to its semimet ($Fe^{II}$,$Fe^{III}$) oxidation level and forms a stable adduct $Fe^{II}Fe^{III}NO_2^-$ [6b]. While there is no evidence that a semimet or metHr is reduced by $NO_2^-$ or $HNO_2$, the observation that the binuclear iron(III,III) complex **1**, a structural analogue of metHr, is reduced by nitrite might be instructive, and we report in this study the results of its investigation.

**Results and Discussion.** – *Equilibrium Studies.* The built-in program of the autotitrator yielded $pK_{a1} = 3.92 \pm 0.15$ and $pK_{a2} = 5.33 \pm 0.10$ for the complex **1** in 95% $D_2O$. The $pK_a$ for nitrous acid in 95% $D_2O$ media was found to be $3.80 \pm 0.10$.

*Stoichiometry and Reaction Products.* Results of several stoichiometric measurements under aerobic conditions yielded an average value of $1.06 \pm 0.04$ for $\Delta[N^{III}]_T/\Delta[Fe_2^{III}]$ ($[N^{III}] = [HNO_2] + [NO_2^-]$). Absorbance measurements at 510 nm established the quantitative (twice that of $[Fe_2^{III}]$) formation of ferroin, $[Fe(phen)_3]^{2+}$. The presence of $NO_3^-$ in the product solution was confirmed by the chromotropic acid test [10]. These observations are in accordance with the net reaction of *Eqn. 1*.

$$[Fe_2^{III}(\mu\text{-}O)(phen)_4(H_2O)_2]^{4+} + NO_2^- + 2\,phen \rightarrow 2\,[Fe(phen)_3]^{2+} + NO_3^- + 2\,H_2O \quad (1)$$

*Kinetics.* The absorbance at 510 nm *vs.* time plots could be well-fitted by the standard first-order growth equations, and $\log_{10}(A_\infty - A_t)$ *vs.* time plots resulted in good

straight lines ($r \geq 0.98$) where $A_\infty$ and $A_t$ stand for the absorbances of the final $[Fe(phen)_3^{2+}]$ ($=2[\mathbf{1}]_{Total}$) and $[Fe(phen)_3^{2+}]_t$ ($=2[\mathbf{1}]_{consumed\ at\ t}$), respectively. The first-order rate constants $k_0$ were evaluated from the slopes of these linear plots. We note here that owing to the slow redox described here, the self-decomposition of **1** to $[Fe(phen)_3]^{2+}$ (reducing equivalents are supplied possibly from the 1,10-phenanthroline present in excess in the solution) is contributing to the overall rate as evidenced from the significant drooping of the $\log_{10}(A_\infty - A_t)$ *vs.* time plots after *ca.* 80% completion of the reactions (*Fig. 2*). The departure from linearity was more pronounced in $D_2O$ media where reactions were slower. Parallel blank experiments were always done, and the absorbances of the solution mixtures at every time were corrected for the background absorptions resulting from the self-decomposition of **1**. The absorptions and the semilog plots thus obtained were well-defined by the corresponding first-order equations for at least up to four half-lives both in $H_2O$ and in $D_2O$ media. Each $k_0$ reported is the average of at least three independent determinations where the coefficient of variation (*CV*) [11] was within a maximum of 3%.

In weakly acidic solution, *viz.* the pH interval chosen for the present investigation, the oxo bridge in **1** is stable though at $pH \leq 2$, **1** slowly decomposes to $[Fe(phen)_3]^{2+}$ that could be identified from its VIS spectra. In all the reported kinetic studies, use of an excess 1,10-phenanthroline not only buffered the reacting solution against any considerable pH drift (mostly within $\pm 0.02$ units) but also ensured quantitative formation of tris(phenanthroline) complexes, $[Fe(phen)_3]^{3+}$ and $[Fe(phen)_3]^{2+}$, from any possible

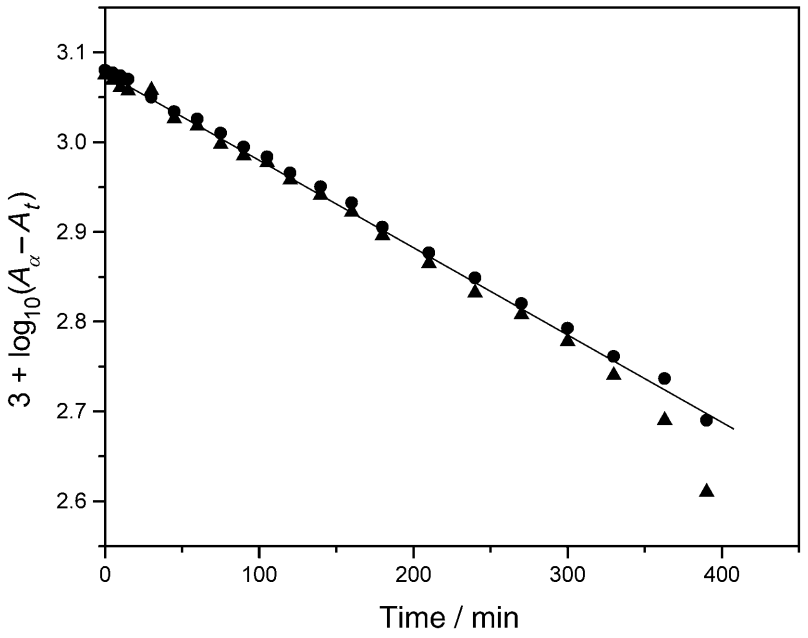


Fig. 2. *Plot of* $log_{10}(A_\infty - A_t)$ vs. *time showing the self-decomposition of the diiron(III,III) complex.* $[Fe_2^{III}] = 0.05$ mM, $[N^{III}]_T = 0.02$M, $C_{phen} = 3.0$ mM. *T* 25.0°, $I = 1.0$M ($NaNO_3$). ▲ = experimental values, ● = corrected values (see text).

transient bis(phenanthroline) intermediates. Otherwise, interpretation of kinetic data would have been difficult, and re-oxidation of $[Fe(phen)_3]^{2+}$ to **1** may be an additional complication as it is well documented that oxidizing agents like chlorite [12], hydrogen peroxide [13], and peroxydiphosphate [14] oxidize $[Fe(phen)_3]^{2+}$ to $\{Fe_2O\}^{4+}$ species, possibly **1**, in absence of any excess 1,10-phenanthroline present in the solution. We note that tris(3,4,7,8-tetramethyl-1,10-phenanthroline)iron(II) catalyzes $HNO_2$ decomposition [15]. No such redox interaction between tris(phenanthroline)iron(II) ($[Fe(phen)_3]^{2+}$) and nitrite was evident as we verified that there is no immediate spectral change of $[Fe(phen)_3]^{2+}$ on mixing 0.10M $NO_2^-$ with 0.10 mM $[Fe(phen)_3]^{2+}$ over a wide pH range (3.2–5.7). Moreover, the spectra of $[Fe(phen)_3]^{2+}$ remained unchanged in presence of nitrite for at least 6 h. We observed a modest increase in rate on increasing $[H^+]$ of the reacting media but the rate remained unchanged within experimental uncertainty (±5%) in presence of $C_{phen} = 3.0–10.0$ mM. Also at a particular pH, the $k_0$ *vs.* $[N^{III}]_T$ plots were linear with statistically insignificant intercept. Constancy of the $k_0$ values on variation of $C_{phen}$ established that no phenanthroline-releasing (from the oxidant) pre-equilibrium was occurring in the solutions. The rate/pH profile suggested that though on increasing pH, more reactive reducing species $NO_2^-$ should enhance the rate [16], concomitant generation of the less reactive hydrolytic deprotonated species of **1** ($pK_{a1}$ and $pK_{a2} = 3.71 \pm 0.05$ and $5.28 \pm 0.10$, resp., at 25.0° and $I = 1.0$M ($NaNO_3$) [4f]) slowed down the reaction at lower acidities [16b][17] (*Table 1*). A few reactions carried out at much less ionic strengths yielded substantially higher $k_0$ values than those at $I = 1.0$M; this possibly demonstrates reactions between oppositely charged species like **1** and its hydrolytic derivatives with $NO_2^-$. However, conceiv-

Table 1. *Some Representative First-Order Rate Constants for the Oxidation of Nitrite by the Dinuclear Iron-(III,III) Complex* **1**. $C_{phen} = 3.0$ mM, *T* 25.0°, $I = 1.0$M ($NaNO_3$).

| pH | $[N^{III}]_T$ [M] | $10^5 k_0$ [$s^{-1}$][a] | | *CV* [%][b] |
|---|---|---|---|---|
| 3.58 | 0.02 | 3.43 | (3.38) | 2.5 |
| 4.06 | 0.02 | 2.71[c] | (2.88) | 2.4 |
| 4.46 | 0.02 | 2.49 | (2.30) | 3.0 |
| 4.97 | 0.02 | 1.81 | (1.68) | 2.2 |
| 5.45 | 0.02 | 1.26 | (1.20) | 2.9 |
| 5.02 | 0.04 | 3.08 | (3.25) | 2.9 |
| 5.05 | 0.06 | 4.69 | (4.78) | 2.6 |
| 5.03 | 0.08 | 6.52[d] | (6.46) | 2.5 |
| 3.50 | 0.04 | 6.96[e] | (6.76) | 2.5 |
| 3.51 | 0.08 | 13.2[f] | (13.5) | 2.5 |
| 3.51 | 0.12 | 20.0 | (20.3) | 2.6 |
| 3.50 | 0.20 | 32.6 | (33.8) | 2.5 |
| 3.49 | 0.04 | 7.03[g] | (6.76) | 2.8 |
| 5.45 | 0.02 | 1.29[g] | (1.20) | 2.7 |
| 3.49 | 0.04 | 6.99[h] | (6.76) | 2.7 |

[a]) $[Fe_2^{III}] = 0.05$ mM unless otherwise stated. Calculated $k_0$ values are given in parentheses. [b]) *CV* was measured using the relation: $CV = sd \cdot 100/x$, where *sd* = standard deviation of the measurements of $k_0$ and $x$ = average $k_0$; see [11]. [c]) $10^5 k_0$ [$s^{-1}$] values are 2.21 and 1.61 at $I = 1.0$M (0.5M NaCl/0.48M $NaNO_3$ and 0.95M NaCl/0.03M $NaNO_3$, resp.) $10^5 k_0$ [$s^{-1}$] = 2.76. [d]) $10^5 k_o$ [$s^{-1}$] values are 4.90 and 6.10 at $I = 0.05$ and 0.01M, resp. [e]) $10^5 k_0$ [$s^{-1}$] = 6.96 at $[Fe_2^{III}] = 0.025$ mM. [f]) $10^5 k_0$ [$s^{-1}$] = 13.2 in presence of 0.20 mM $[Fe(phen)_3]^{2+}$. [g]) In presence of 6.0 mM phen. [h]) The reaction was carried out in presence of purified $N_2$.

able rate retardation was noticed when $NaNO_3$ was partially substituted by NaCl at $I=1.0$M ($NaNO_3+NaCl$; see *Table 1*). We also verified that the $k_0$ values remained constant (within 5%) on a four-fold variation in complex concentration (0.025–0.1 mM), when the reactions were carried out in presence of added $[Fe(phen)_3]^{2+}$ (up to 0.3 mM), on variation of the monitoring wavelength in the range 440–530 nm, when the reaction media were purged with purified $N_2$, or when stray light was excluded by running the reaction in closed containers the walls of which were covered by japan black. *Table 1* summarizes some representative $k_0$ values.

The observed kinetics may be well-described by *Scheme 1* (*Eqns. 5–7*) along with the known equilibria of *Eqns. 2–4*.

$$\underset{\mathbf{1}}{\left[Fe_2^{III}(\mu\text{-}O)(phen)_4(H_2O)_2\right]^{4+}} \underset{pK_{a1}=3.71}{\overset{K_{a1}}{\rightleftharpoons}} \underset{\mathbf{2}}{\left[Fe_2^{III}(\mu\text{-}O)(phen)_4(H_2O)(OH)\right]^{3+}} + H^+ \tag{2}$$

$$\underset{\mathbf{2}}{\left[Fe_2^{III}(\mu\text{-}O)(phen)_4(H_2O)(OH)\right]^{3+}} \underset{pK_{a2}=5.28}{\overset{K_{a2}}{\rightleftharpoons}} \underset{\mathbf{3}}{\left[Fe_2^{III}(\mu\text{-}O)(phen)_4(H_2O)(OH)_2\right]^{2+}} + H^+ \tag{3}$$

$$HNO_2 \rightleftharpoons NO_2^- + H^+;\ pK_a=3.00\ [16b][18] \tag{4}$$

*Scheme 1*

$$\mathbf{1} + NO_2^- \xrightarrow{k_1} \text{products} \tag{5}$$

$$\mathbf{2} + NO_2^- \xrightarrow{k_2} \text{products} \tag{6}$$

$$\mathbf{3} + NO_2^- \xrightarrow{k_3} \text{products} \tag{7}$$

In *Scheme 1*, we did not consider any protonation equilibrium of $HNO_2$ generating $NO^+$ (*Eqn. 8*) or disproportionation equilibrium of $HNO_2$ generating NO and $NO_2$ (*Eqn. 9*). A reaction path involving NO would require a $[HNO_2]^2$ term in the rate law and $NO^+$ requires a third-order term $[Fe_2^{III}][HNO_2][H^+]$. The equilibrium constants of these reactions are small, and that might be a major reason for not obtaining the reactivities, if any, of these species. We, thus, used $[N^{III}]_T=[HNO_2]+[NO_2^-]$.

$$HNO_2 + H^+ \rightleftharpoons NO^+ + H_2O;\quad K=3.0\cdot10^{-7}\ [19] \tag{8}$$

$$2\ HNO_2 \rightleftharpoons NO^+ + NO_2 + H_2O;\quad K=6.0\cdot10^{-6}\ [20] \tag{9}$$

*Scheme 1* leads to the rate law of *Eqn. 10* where $k_0$ is defined by *Eqn. 11*, $\alpha_1$ (*Eqn. 12*) is the fraction of the total Fe-complex present as **1**, and $\alpha_2$ (*Eqn. 13*) is the fraction of total nitrite present as $NO_2^-$ ($pK_a$ of $HNO_2$ being 3.00 at 25.0°, $I=1.0$M) [16b][18a].

$$k_0[H^+]^2/([N^{III}]_T\alpha_1\alpha_2) = k_1[H^+]^2 + k_2K_{a1}[H^+] + k_3K_{a1}K_{a2} \tag{10}$$

$$\text{Rate} = -d[Fe_2^{III}]/dt = 2d[Fe(phen)_3^{2+}] = k_0[Fe_2^{III}] \quad (11)$$

$$\alpha_1 = 1/(1+K_{a1}/[H^+]+K_{a1}K_{a2}/[H^+]^2) \quad (12)$$

$$\alpha_2 = K_a/(K_a+[H^+]) \quad (13)$$

The left-hand side of *Eqn. 10* when plotted against $[H^+]$ resulted in a good polynomial fit (*Fig. 3*, $r > 0.98$), second-order in $[H^+]$, whence the second-order rate-constants $k_1$, $k_2$, and $k_3$ (*Table 2*) were calculated from the corresponding coefficients by using the known $K_{a1}$ and $K_{a2}$. These rate constants regenerate all the experimental $k_0$ values quite satisfactorily (*Table 1*).

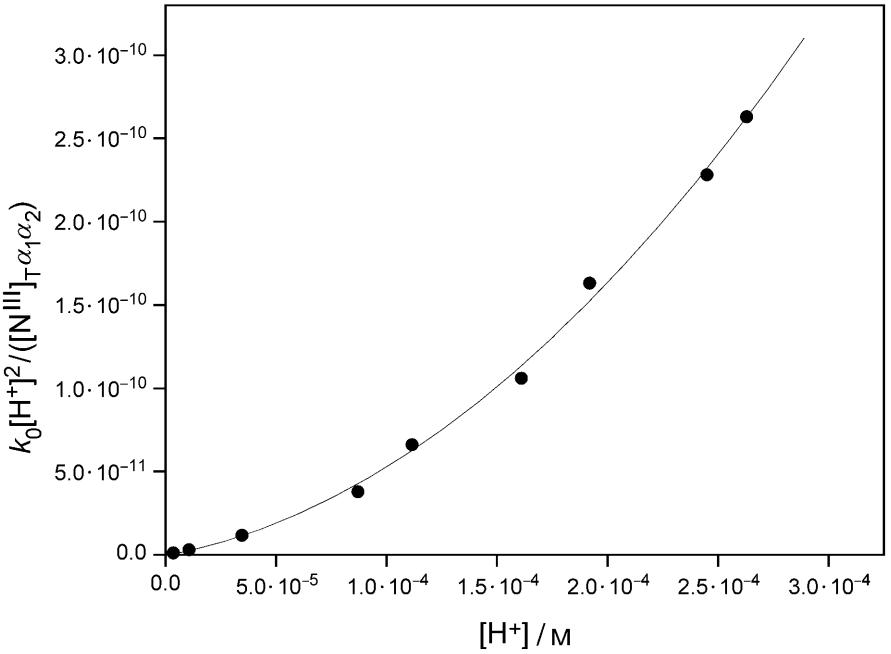


Fig. 3. *Plot of left-hand side of* Eqn. 10 vs. *$[H^+]$*

Table 2. *Second-Order Rate Constants*[a]) *for the Oxidation of Nitrite by the Dinuclear Iron(III,III) Complex*. *T* 25.0°, $I = 1.0$M ($NaNO_3$), $C_{phen} = 3.0$ mM.

| Reaction path | $10^4$ Rate constant [$M^{-1}s^{-1}$] in $H_2O$ | $10^4$ Rate constant [$M^{-1}s^{-1}$] in 95% $D_2O$ |
|---|---|---|
| $k_1$ (**1**+$NO_2^-$) | 30.0±2.2 | 27.0±2.4 |
| $k_2$ (**2**+$NO_2^-$) | 10.0±0.7 | 6.0±0.3 |
| $k_3$ (**3**+$NO_2^-$) | 3.0±0.04 | 0.90±0.05 |

[a]) These *k* values are for overall reactions and are, therefore, equal to twice the rate constant for *Eqn. 18* shown in *Scheme* 3.

An alternative to *Scheme 1* that also fits the experimental observations is shown in *Scheme 2* (*Eqns. 14–16*) involving only $HNO_2$ and not $NO_2^-$.

*Scheme 2*

$$\mathbf{1} + HNO_2 \xrightarrow{k_1'} \text{products} \quad (14)$$

$$\mathbf{2} + HNO_2 \xrightarrow{k_2'} \text{products} \quad (15)$$

$$\mathbf{3} + HNO_2 \xrightarrow{k_3'} \text{products} \quad (16)$$

The derived rate law for *Scheme 2* is given by *Eqn. 17*. The polynomial of *Eqn. 17* may be solved in the usual manner resulting in $k_1' = (5.9 \pm 0.3) \cdot 10^{-3}$, $k_2' = (6.2 \pm 0.4) \cdot 10^{-3}$, and $k_3' = (2.7 \pm 0.2) \cdot 10^{-2} M^{-1} s^{-1}$. Of particular note in this result are the similar values of $k_1'$ and $k_2'$ and the much higher value of $k_3'$. We find that these values are not kinetically acceptable though it is a good numerical solution. Indeed, $NO_2^-$ is a much stronger coordinating ligand than $HNO_2$ and present in a much higher concentration than $HNO_2$ in the entire pH range studied ($[NO_2^-]_{min} > 3[HNO_2]$, $[NO_2^-]_{max} > 99[HNO_2]$); thus, why $HNO_2$ will be reactive in such a situation? The neutral species $HNO_2$ is not expected to swamp the reactivity of $NO_2^-$ by its own. Moreover, for the occurrence of perfect inner-sphere paths, a direct bonding between the iron and $HNO_2$ *via* hydroxo/aqua ligands is required what is not possible as $N^{III}$ has no low-lying vacant acceptor orbitals. Superior reactivity of hydroxo paths thus may not be possible. We thus prefer to consider only *Scheme 1* for the further discussion.

$$K_a k_0 [H^+]/([N^{III}]_T \alpha_1 \alpha_2) = k_1'[H^+]^2 + k_2' K_{a1}[H^+] + k_3' K_{a1} K_{a2} \quad (17)$$

*Mechanism.* The observed trend of evaluated second-order rate-constants $k_1 > k_2 > k_3$ demonstrates that protonated oxidants are more reactive than their deprotonated conjugate-base analogues – a trend that is well-accepted in redox reactions with polyprotic redox partners [17c][21]. In the investigated pH range, the linearity of $k_0$ on $[N^{III}]_T$ suggests weak adduct formation, if any, between the $Fe^{III}$ dimer and $NO_2^-$. Any possible pre-equilibrium binding of $NO_2^-$ with $Fe^{III}$ in the present situation renders the estimated maximum value for the pre-equilibrium constant ($K_i$) around $10^1$, holding the inequality $K_i[NO_2^-] \ll 1$ with no obvious lower limit. We note here that the bare $Fe^{3+}$ binding with $NO_2^-$ to form mono- ($Fe(NO_2)^{2+}$), di- ($Fe(NO)_2)_2^+$), or trinitro species ($Fe(NO_2)_3$) is much stronger (overall stability constants $\beta_i$'s ($i = 1-3$) are of the order $10^2$, $10^3$, and $10^5$, resp.) [22].

Replacement of $Fe^{III}$-bound $H_2O$ or $OH^-$ by $NO_2^-$ in the present investigation is thus found to be weak, at best. The estimated small pre-equilibrium constants, we find, could not be related to the ion pairing as in presence of added $Cl^-$, the reaction rate decreases. Rate retardation in presence of $Cl^-$ ($Br^-$ is found to be almost innocent, *Table 1*) may be due to a competitive process where nonreducing chloride, present in large excess, competes with $NO_2^-$ for the adduct formation.

It is also well-documented that solutions of $[Fe_2^{III}L_4Cl_2(\mu\text{-}O)]^{4+}$ [23] rapidly aquate to generate $[Fe_2^{III}L_4(H_2O)_2(\mu\text{-}O)]^{4+}$ and also instantaneously produce $[Fe_2^{III}L_4(SCN)_2(\mu\text{-}O)]^{2+}$ on adding a KSCN solution (L = 2,2′-bipyridine or 1,10-phenanthroline) [23][24]. These observations clearly indicate the labile nature of the monodentate ligands, *viz*. $Cl^-$ and $H_2O$ bound to each $d^5$ high-spin $Fe^{III}$ center.

The overall redox in this study is a net $2e^-$ transfer and is expected to proceed in steps to avoid the prohibitive *Frank–Condon* barrier. We like to assign the rate-determining step to a $1e^-$ transfer yielding the respective $Fe^{II}-O-Fe^{III}$ dimers that immediately collapse either by aquation to $Fe^{II}$ and $Fe^{III}$ monomers or by further reduction to $Fe^{II}$ monomers. The $Fe^{III}$ monomer $[Fe(phen)_2(H_2O)_2]^{3+}$ is further reduced to the $Fe^{II}$

monomer $[Fe(phen)_2(H_2O)_2]^{2+}$ that rapidly forms ferroin ($[Fe(phen)_3]^{2+}$) in the presence of excess phenanthroline as used in our study. It is known that $[Fe(phen)_3]^{3+}$ is almost instantaneously reduced to ferroin by $HNO_2$ [25]. $[Fe(phen)_2(H_2O)_2]^{3+}$ is expected to react even faster with nitrite. Formation of ferroin from $Fe^{2+}$ and excess phen is also known to be a fast reaction [26]. Inner-sphere reduction of $[Fe(phen)_3]^{3+}$ by nitrite should be slow since substitution at this low-spin $d^5$ $Fe^{III}$ complex is slow, contrary to the situation of the diaqua derivative as the $d^5$ high-spin diaqua species would be labile to substitution [27]. Even with $[Fe(phen)_3]^{3+}$, the outer-sphere reduction should be fast as estimated by the *Marcus* relation [28]. Thus, the calculated rate constant for a $1e^-$ outer-sphere reduction of $[Fe(phen)_3]^{3+}$ by $NO_2^-$ is *ca.* $3 \cdot 10^3\ M^{-1}\ s^{-1}$. The reaction of $[Fe(phen)_3]^{3+}$ with $HNO_2$ is reported to be reversible with the $1e^-$ reduction rate of $[Fe(phen)_3]^{3+}$ being *ca.* $30\ M^{-1}\ s^{-1}$ [25]. The much higher rate constant for the reduction as calculated by the *Marcus* equation may be due to a change in the reactive species, $NO_2^-$ instead of $HNO_2$.

Within the time period for the kinetic studies, the self-decomposition of complex **1** is little (though considered in measuring $k_0$ values). The $\{Fe_2O\}^{4+}$ core unit in **1** or similar species is stable, the stability arises from the superexchange of the two $d^5$ high-spin $Fe^{III}$ centers through the oxo bridge [29]. However, the high-spin $Fe^{II}$ and $Fe^{III}$ must be less strongly bound to $O^{2-}$ since both oxidation states having two antibonding electrons are directed towards the formal bond axes that would impart weakening of the $Fe^{II}-O-Fe^{III}$ and $Fe^{II}-O-Fe^{II}$ bonds, both of which are expected to be rapidly broken by aquation, or by further reduction (*Scheme 3*, *Eqns. 18–22*). In fact, the oxo bridge in the mixed-valent system $Fe^{II}-O-Fe^{III}$ is rather uncommon [2d][30] and in general putative outside a protein environment. It is thus becoming justified that complete reduction of the $\{Fe_2O\}^{4+}$ units involves several steps; the only rate-determining step would be the one-electron transfer, $\{Fe_2O\}^{4+} + e^- \rightarrow \{Fe_2O\}^{3+}$ (*Eqn. 18*) and all subsequent steps (*Eqns. 19–22*) are kinetically silent.

*Scheme 3*

$$\{Fe^{III}-O-Fe^{III}\}^4 + NO_2^- \xrightarrow[k]{\text{slow}} \{Fe^{II}-CO-Fe^{III}\}^{3+} + NO_2 \tag{18}$$

$$\{Fe^{II}-O-Fe^{III}\}^{3+} + H^+ \rightleftharpoons \{Fe^{II}-\underset{H}{O}-Fe^{III}\}^{4+};\ \text{fast} \tag{19}$$

$$\{Fe^{II}-\underset{H}{O}-Fe^{III}\}^{4+} + NO_2^- \xrightarrow{\text{fast}} 2\ Fe^{II} + NO_2 + H_2O \tag{20}$$

$$Fe^{II} + 3\text{phen} \rightarrow [Fe(phen)_3]^{2+};\ \text{fast} \tag{21}$$

$$2\ NO_2 + H_2O \rightarrow NO_3^- + HNO_2 + H^+;\ \text{fast} \tag{22}$$

In an alternate description of reaction sequences, a strong pre-equilibrium binding of $NO_2^-$ with the $Fe^{III}$ dimer and subsequent reaction with a second $NO_2^-$ according to *Scheme 4* (*Eqns. 23* and *24*) would lead to the rate law of *Eqn. 25*.

Nitrite redox reactions leading to nitrate products with second-order nitrite dependence have been identified in several instances [31]. However, for $K[NO_2^-] \gg 1$, the observed kinetics along with the first-order dependence on $[N^{III}]_T$ could be explained with the rate law of *Eqn. 25*. For $K[NO_2^-] \gg 1$, it requires $(K)_{minimum}$ as high as

around $10^3$. We, however, found no second-order dependence (*vide supra*) in the redox we are studying that clearly removes any possibility of strong pre-equilibrium binding of $NO_2^-$ with $Fe_2^{III}$, and thus, *Scheme 4* is not an alternative to *Scheme 3*.

*Scheme 4*

$$Fe_2^{III} + NO_2^- \overset{K}{\rightleftharpoons} Fe_2^{III} \cdot NO_2^- \tag{23}$$

$$Fe_2^{III} \cdot NO_2^- + NO_2^- \overset{k}{\rightarrow} \text{products} \tag{24}$$

$$\text{Rate} = kK[Fe_2^{III}]_0[NO_2^-]^2/(1+K[NO_2^-]) \tag{25}$$

The immediate $1e^-$ oxidation of $NO_2^-$ results in $NO_2$ which is known to disproportionate quickly in aqueous solution producing $NO_3^-$ and $NO_2^-$ [32]. The $1e^-$-reduced Fe-dimer $\{Fe^{II}-O-Fe^{III}\}^{3+}$ should immediately take up a proton (either from the reaction media or from the $NO_2$ disproportionation, *cf. Eqn. 22*) as the basicity of the oxo bridge is expected to increase tremendously in comparison to the $\{Fe^{III}-O-Fe^{III}\}^{4+}$ dimer. Precedences of such differences in basicities of the oxo bridges in di- or multinuclear higher-valent Mn complexes are well-established [33], and these differences are a key feature in redox steps of the Kok cycle in PS II [34]. The possibility of protonation at the oxo bridge of **1** is ruled out as during its synthesis from $Fe(NO_3)_3 \cdot 9H_2O$ and 1,10-phenanthroline in a 1:2 ratio, a pH as low as *ca.* 1.9 is maintained. We find that the available evidences on hemerythrin [9c][35] strongly suggest that protonation of the oxo bridge is not a pre-requisite for a $1e^-$ reduction of the diferric site in methemerytrin. Protonation at some point after $1e^-$ reduction would be favored due to the expected increase in basicity of the oxo bridge that could remove thermodynamic and/or kinetic barriers to further reduction [3c]. Proton-coupled electron transfer is the basic mechanism for the bioenergetic redox conversions in proteins [36]. Protonation of $\{Fe_2O\}^{3+}$ (*Eqn. 19*) thus remains an essential step in the overall reaction. It should be noted that instead of the disproportionation of $NO_2$ to $NO_3^-$ and $NO_2^-$, a direct electron transfer from $NO_2$ to $\{Fe_2O\}^{3+}$ leading to products *via* the fast hydrolysis of $NO_2^+$ thus generated can not be ruled out on principle. Oxidation of $NO_2$ by higher-valent metal complexes are sometimes proposed [16a][37]. Adopting an inner-sphere pathway for the rate-determining $1e^-$ transfer generating $\{Fe_2OH\}^{4+}$ and $NO_2$, subsequent immediate electron transfer from $NO_2$ to $\{Fe_2OH\}^{4+}$ is not a remote possibility as, due to the close proximity of $\{Fe_2OH\}^{4+}$ and $NO_2$, the latter may transfer one electron to the $Fe^{III}$ center before diffusing into the bulk solvent for its disproportionation.

Complex **1** is a mild oxidant, its $1e^-$ reduction potential is $-0.18$ V *vs.* NHE [4f]. One-electron oxidation of $NO_2^-$ to $NO_2$ is extremely endothermic, $-1.04$ V [38]. The overall one-electron exchange of *Eqn. 26* is thus thermodynamically much unfavorable; the equilibrium constant $K$ for this $1e^-$ redox is computed to be very small (*ca.* $10^{-20}$) which is not in agreement with the forward rate constant for *Eqn. 26*, assuming $k_b$ has a diffusion-control limit ($10^{10}\ M^{-1}\ s^{-1}$). Using the value of $k_f$ of the order $10^{-4}$ to $10^{-3}\ M^{-1}\ s^{-1}$ (*Table 2*) yields a $K$ of the order $10^{-14}$ to $10^{-13}$ for *Eqn. 26* which allows to estimate a comparatively less endothermic $1e^-$ oxidation of $NO_2^-$, around $-0.60$ V. It may be concluded that coordination of $NO_2^-$ to the $Fe^{III}$ center increases its oxidizability.

$$Fe_2^{III} + NO_2^- \underset{k_b}{\overset{k_f}{\rightleftharpoons}} Fe^{III}Fe^{II} + NO_2 \tag{26}$$

To collect further information on the proposed mechanism involving the necessity of a proton-coupled electron transfer as described in *Eqns. 18* and *19* of *Scheme 3*, we performed several kinetic runs in $H_2O$ and $D_2O$ media, and we found a detectable lowering in rate in the latter cases. Variations in rate resulting from substitution of $D_2O$ for solvent $H_2O$ are expected to be slight for simple electron-transfer reactions, but a substantial rate retardation is expected when such a transfer is coupled with the movement of protons, which are in equilibrium with solvent protons [37][39]. It is noticeable that the plots of $k_0$ *vs.* the mol fraction of $D_2O$ are linear (*Fig. 4*, $r > 0.98$), and the linear plots are indicative of the transfer of just one single proton in the rate-determining step of the redox process [40]. Well-documented rate retardation in $D_2O$ media compared to that in $H_2O$ for the deoxygenation process of the oxygen binding to hemerythrin is mechanistically reminiscent [41]. We are thus able to state that, besides having a decrease in the endothermicity of $NO_2^-$ oxidation by its coordination $Fe^{III}$ which increases the thermodynamic ability of $NO_2^-$ oxidation, simultaneous proton/electron transfer is another driving force for the redox of **1**. Additionally, the exceptional stability of the low-spin $[Fe(phen)_3]^{2+}$ formed as the sole Fe-product also drives the reaction to completion.

The second-order rate constants are also determined in 95% $D_2O$ media and compared with those in $H_2O$ (*Table 2*). The observed difference in kinetic isotope effect is prominent at higher pH ($k_3$ is mostly affected and $k_1$ is least affected). A hydroxo ligand is much more basic than $H_2O$ [42] and makes the Fe-centers less electron accepting; this results in increasing basicity of the oxo bridges in the order **3** > **2** > **1**. A similar trend in isotope effects was also earlier observed in the reduction of $[Mn_2^{IV}(\mu\text{-O})_2(\mu\text{-MeCO}_2)$-

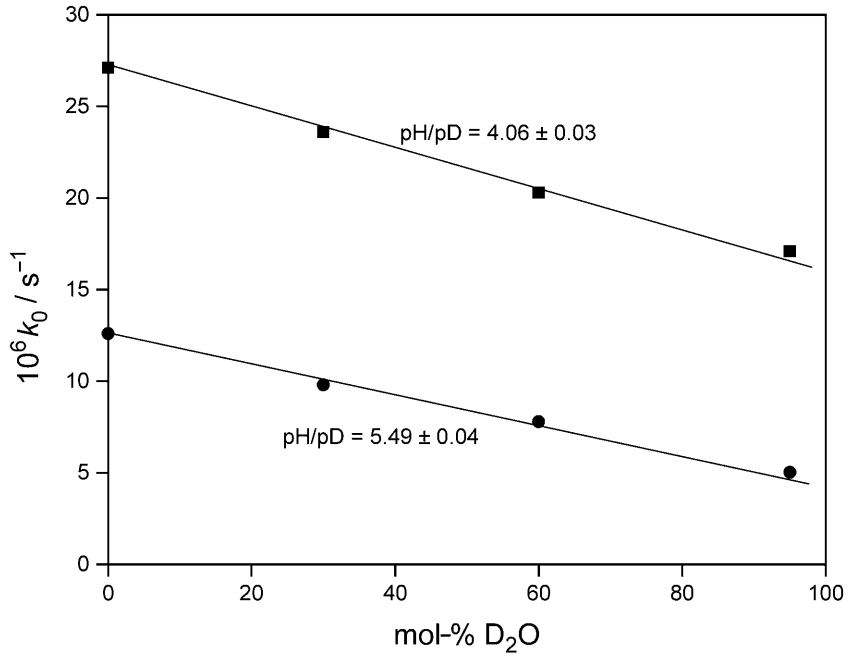


Fig. 4. *Effect of mol-% $D_2O$ on $k_0$* [$s^{-1}$]. $[Fe_2^{III}] = 0.05$ mM, $[N^{III}]_T = 0.02$M, $C_{phen} = 3.0$ mM, $T$ 25.0°, $I = 1.0$M ($NaNO_3$).

$(bipy)_2(H_2O)_2]^{3+}$ ($MeCO_2H$ = acetic acid, bipy = 2,2′-bipyridine) and its hydrolytic derivatives with hydroxylamine [43].

The oxo bridge in complex **1** is not protonated though oxo-bridge protonation must occur while one Fe-center is reduced to $Fe^{II}$. We thus formally separate these two acts: the rate-determining $1e^-$ reduction and then a very fast oxo-bridge protonation[1]). The $Fe^{III}$ dimer **1** is a mild oxidant [4f], and we now observed that its one-electron potential is independent on the working pH range 3.5–5.5 where all its proton-dependent species are available. This indicates species **1**–**3** are almost equally oxidizing which in turn predicts that the reactions of *Eqns. 5–7* are equally unfavorable from a purely thermodynamic consideration. Yet we find substantial differences in the reactivities of **1**–**3** with $NO_2^-$, and more importantly, the kinetic isotope effect is most observable in the $k_3$ path where the basicity of the oxo bridge of the one-electron reduced dimer, *viz*. $[(phen)_2(OH)Fe^{III}OFe^{II}(phen)_2(OH)]^+$ is highest. This clearly demonstrates that oxo-bridge protonation is the key step in the proposed mechanism.

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## Experimental Part

*Materials.* The complex salt $[Fe_2(\mu\text{-}O)(phen)_4(H_2O)_2]X_4\cdot 5H_2O$ ($X = NO_3^-$ or $ClO_4^-$) was prepared following a reported method [7], and its purity was checked by elemental analyses as well as by its reported optical spectra. The crystals obtained were found to be sufficiently pure. Stock solns. of $NaNO_2$ were prepared by dissolving solid $NaNO_2$ (G. R. grade; *E. Merck*), recrystallized from hot aqueous EtOH and standardized by $KMnO_4$ titration [44] as well as by spectrophotometry at 355 nm ($\varepsilon = 23.3\ M^{-1}\ cm^{-1}$) [45]. Both yielded closely similar results (within 3%). These solns. (0.05–0.50M) were spectrophotometrically found to be stable for at least 24 h at *ca.* 10° and at pH > 6.0. Solns. of recrystallized $NaNO_3$ and $NaClO_4$ (both of G. R. grade; *E. Merck*) were standardized by cation-exchange resin as described earlier [43]. The 1,10-phenanthroline (G. R. grade; *E. Merck*) was used without further purification. Tris(phenanthroline)iron(III) nitrate ($[Fe(phen)_3](NO_3)_3$) and tris(phenanthroline)iron(II) nitrate ($[Fe(phen)_3](NO_3)_2$) were prepared and standardized by using literature procedures[46][47]. $D_2O$ (99.9 atom-% D; *Aldrich*) was used for the preparation of all the solns. when kinetic isotope effects were measured. Sulfanilic acid and napthalen-1-amine were from *E. Merck* (G. R. grade), and the disodium salt of 1,8-hydroxynaphthalene-3,6-disulfonic acid (= chromotropic acid; *Sigma*, reagent grade) was used as received. Chromium(II)-scrubbed $N_2$ gas and doubly distilled deionized $H_2O$ were used. All other chemicals were of reagent grade.

*Physical Measurements and Kinetics.* All absorbances and optical spectra were recorded with a *Shimadzu 1601 PC* spectrophotometer in 1.00-cm quartz cells. The kinetic traces were monitored *in situ* in the 'kinetic mode' of the instrument at 510 nm, the VIS-absorbance maximum of the final iron species, $[Fe(phen)_3]^{2+}$ [48], in the electrically controlled thermostated (25.0 ± 0.1)° cell housing (*CPS-240A*) as described earlier. Excess of 1,10-phenanthroline concentration, $C_{phen}$ (= [Hphen$^+$] + [phen]), in the range 3–10 mM, was used in all the kinetic runs. $NaNO_2$ Solns. were directly injected into the spectrophotometer cells containing all other components of the reaction mixture. The final concentrations of the diiron complex and the reducing agent were achieved after mixing which was immediately followed by automatic monitoring of the change in absorb-

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[1]) Sometimes PCET (= proton-coupled electron transfer) is referred to a single chemical reaction step involving concerted transfer of both a proton and an electron. PCET is thus differentiated from stepwise pathways that involve mechanistically distinct electron- and proton-transfer steps. 'Concerted' thus indicates the absence of an intermediate but does not imply synchronous transfer [36c][36d]. In this study, we propose that the electron transfer is slow followed by a very fast proton transfer (acid-base reaction) and thus though these steps are mechanistically distinct, one can also call them concerted. The oxo-bridge mixed-valent $Fe^{III}$. $Fe^{II}$ dimer is putative outside a protein environment, and we could not gather any direct spectral or kinetic evidence on the intermediate generation of any such mixed-valent species during the reduction of **1**. All steps beyond *Eqn. 18* are fast (*Scheme 3*).

ance with time. To minimize redox decomposition of $HNO_2$ to NO and $NO_2$, we used capped quartz cells with minimum vacant space left as the decomposition of $HNO_2$ in acidic media depends strongly on the NO escape rate [49]. Moreover, we used low $[N^{III}]_T$, and in our experimental pH range (3.49–5.45), free $HNO_3$ concentration is low. The measured average stoichiometry of the reaction (1.06, see *Results and Discussion*) is only marginally higher than the ideal value (1.00) that indicates only slight loss of $[N^{III}]_T$. Measurement of soln. pH values and calibration of pH electrodes (*Orion* pH-meter, model *710 A*) were described earlier in detail [50]. For reactions in $D_2O$, pD was calculated as $pD = (pH)_{measured} + 0.40$ [51] where $(pH)_{measured}$ is the pH-meter reading in $D_2O$. Nitric acid (99 atom-% D; *Aldrich*) and solid NaOH dissolved in $D_2O$ were used for this purpose. Excess reducing agent, $[N^{III}]_T$ ($= [HNO_2] + [NO_2^-]$), 0.01–0.15 mM, was maintained over the complex (generally 0.05 mM) in all the kinetic runs. The first-order observed rate constants $k_0$ were measured from the least-squares slopes of $\ln(A_\infty - A_t)$ *vs.* time plots. Most of the reported $k_0$ values are at 25.0° and at $I = 1.0$M ($NaNO_3$).

*Equilibrium Measurements.* Acid dissociation constants of the complex **1** and nitrous acid were determined by pH-metric titration with a *Metrohm 736 GP Titrino* autotitrator in 95% $D_2O$ media as described earlier [4f]. The acid dissociation constant of nitrous acid was measured by dissolving solid $NaNO_2$ in $D_2O$ and quickly titrating the soln. with $DNO_3$ to avoid acid-induced decomposition of nitrous acid.

*Stoichiometry and Reaction Products.* The stoichiometry of the overall reaction was determined under kinetic conditions ($[N^{III}]_T > [Fe_2^{III}]$) by measuring the reaction product, *viz*. $[Fe(phen)_3]^{2+}$, and the unreacted $[N^{III}]$. The UV/VIS spectra of product solns. confirmed the quantitative formation ($98 \pm 3\%$) of $[Fe(phen)_3]^{2+}$ as the sole Fe-product. Excess $[N^{III}]$ left after the completion of the reactions was measured colorimetrically [52]. For this purpose, $Fe_2^{III}$ in the concentration range 0.05–0.20 mM were treated with $[N^{III}]_T$ in 2–4 times of $[Fe_2^{III}]$ at pH 3.5–4.0. After completion of the reactions as indicated by the quantitative generation of $[Fe(phen)_3]^{2+}$ measured at 510 nm ($\varepsilon = 1.11 \cdot 10^4$ M$^{-1}$ cm$^{-1}$) [48] after necessary dilution, excess $Fe(ClO_4)_2$ and $NaClO_4$ solns. were added into the soln. mixtures. Excess $Fe^{2+}$ quantitatively removed 1,10-phenanthroline forming $[Fe(phen)_3]^{2+}$ that was precipitated from the soln. as its perchlorate salt due to its poor solubility and removed by filtration. The soln. mixtures were then appropriately diluted and treated with sulfanilic acid and napthalen-1-amine to form the characteristic red dye. The removal of $[Fe(phen)_3]^{2+}$ as well as excess 1,10-phenanthroline was necessary to avoid their interference. The absorbance of the dye was measured at 520 nm, and the concentration of unreacted $N^{III}$ was obtained from a calibration curve (exper. $\varepsilon^{520} = 4.1\ (\pm 0.03) \cdot 10^4$ M$^{-1}$cm$^{-1}$, in close agreement with the reported $\varepsilon^{520} = 4.0 \cdot 10^4$ M$^{-1}$ cm$^{-1}$) [52].

The $NO_3^-$ produced in the title redox was qualitatively tested by the chromotropic acid method [10]. For this purpose, the perchlorate salt of $Fe_2^{III}$ was treated with excess $N^{III}$. After completion of the reaction, $[Fe(phen)_3]^{2+}$ and 1,10-phenanthroline were removed by adding excess $Fe(ClO_4)_2$ as described above. Excess nitrite in the soln. was removed by sulfite/urea soln. The chromotropic acid reagent was then added followed by conc. $H_2SO_4$ soln. A yellow color developed that qualified the presence of $NO_3^-$; we verified [10] that both $Fe^{2+}$ and $ClO_4^-$ do not interfere.

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