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THE INTERACTION OF IRON COMPLEXES WITH SMALL NITROGEN-CONTAINING MOLECULES AND IONS

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CONTENTS

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ABBREVIATIONS

A	polyaminocarboxylic acid
acacen	*N*,*N*′-ethylenebis(acetylacetonylideneiminato)(−1) anion
AMBM	2-aminomethylbenzimidazole
[*n*]aneN_4	tetraaza macrocyclic ligand with *n*-membered chelate ring
Ar	aryl group
bm	benzylmercaptan (2-mercaptoethanol)
BMEA	*N*,*N*-bis(2-benzimidazolylmethyl)ethanolamine
bpy	2,2′-bipyridine
18-C-6	18-crown-6 ether (1,4,7,10,13,16-hexaoxacyclo octadecane)
Cp	cyclopentadienyl(−1) anion
DMF	dimethylformamide
dmdtc	dimethyldithiocarbamate(−2) anion
DMSO	dimethylsulfoxide
edta	ethylenediaminetetraacetate(−4) anion
1-FIQTSC	1-formylisoquinoline thiosemicarbazone
2-FQTSC	2-formylquinoline thiosemicarbazone
Hb^+	methemoglobin
HMBM-H	2-hydroxymethylbenzimidazole(−1) anion
HMBT-H	2-hydroxymethylbenzothiazole(−1) anion
HMPA	hexamethylphosphoric triamide
iah	isonicotinic acid hydrazide
L	ligand
Mb^+	metmyoglobin
Me	methyl
1-Meim	1-methylimidazole
MeOH	methanol
N-bipyO	2,2′-bipyridine *N*-oxide
N-Meim	*N*-methylimidazole
4-Mepy	4-methylpyridine
n_{app}	apparent electron number

5-nitroOEP	5-nitrooctaethylporphyrin(−2) anion
N-phenO	1,10-phenanthroline *N*-oxide
OEC	octaethylchlorin(−2) anion
OEiBC	octaethylisobacteriochlorin(−2) anion
OEP	octaethylporphyrin(−2) anion
Pc	phthalocyanine(−2) anion
Ph	phenyl
phen	1,10-phenanthroline
pip	piperidine
Por	porphyrin(−2) anion
Pr-i	isopropyl group
py	pyridine
R	methyl, ethyl, and phenyl groups
saldien	[α,α′-[imino-bis(di-methylenenitrilo)]di-*o*-cresolato](−2) anion
salen	*N*,*N*′-ethylene-bis(salicylideneiminato)(−2) anion
salmedien	[α,α′-[methylimino-bis(dimethylenenitrilo)]di-*o*-cresolato(−2) anion
salphen	*N*,*N*′-phenylene-bis(salicylideneiminato)(−1) anion
THF	tetrahydrofuran
TML	tetradentate macrocycle formed from 2,6-diaminopyridine and acetylacetone(−2) anion
TMP	3,4,7,8-tetramethylphenanthroline
TmPP	*meso*-tetrakis(2,4,6-trimethylphenyl) porphyrin(−2) anion
TMpyP	*meso*-tetrakis(*N*-methyl-4-pyridyl) porphyrin(+2) cation
TpivPP	*meso*-α,α,α,α-tetrakis(*o*-pivalamidophenyl) porphyrin(−2) anion
TPP	*meso*-tetraphenylporphyrin(−2) anion
TPPS	*meso*-tetrakis(*p*-sulfonatophenyl)porphyrin(−4) anion
Ts	tosyl group
X	halide ion or nitrogen species serving as a ligand

A. INTRODUCTION

The biochemistry of iron is replete with examples of iron compounds that interact with oxynitrogen and hydridonitrogen species. This was emphasized recently in a symposium on the chemistry of nitrogen at a 1990 American Chemical Society meeting. Much of this interest has primarily focused on the development of models for nitrate and nitrite reductase since iron is at the active sites of both reductases [1–5]. Such development will require a good understanding of the ways in which small nitrogen-containing ions and molecules might interact with the iron in the biomolecules. It was felt that a literature survey of the interactions that such nitrogen species have with relatively simple iron complexes would assist in the development of the complex biological models.

The interaction of small nitrogen-containing species with iron compounds is not only of importance for developing reductase models, but is also of interest in a number of other areas. Some examples are:

(1) Nitrates and nitrites are direct causative agents for the disease methemoglobinemia which has been especially dangerous for infants. This results from the oxidation of the iron(II) center in hemoglobin, destroying its oxygen-carrying ability [6,7].

(2) The iron–nitrosyl group has found considerable use as an ESR and resonance Raman probe to study heme and non-heme proteins [8–13].

(3) NO is a gaseous effluent of coal-fired power plants, and certain aminopolycarboxylic acid iron complexes in aqueous solution are able to absorb NO and catalyze its reactions [14,15].

(4) In the curing of certain meats, sodium nitrite reacts with the iron porphyrin complex in the myoglobin to form an Fe–NO bond [16–18]. The nitrite may inhibit the growth of microbes, such as *Clostridium botulinum*, in the meat by reacting with the Fe–S cluster in Fe–S proteins such as ferredoxin [19].

(5) The complex mixture making up radioactive defense nuclear waste contains significant amounts of iron(III) and nitrate and nitrite salts. Heating the mixture with added formate salts and borosilicate glass frit in order to encapsulate the waste into glass possibly causes a number of reactions between oxynitrogen species and iron compounds. These can influence the redox state of the glass [20–22].

(6) Nitrite is effective in preventing the corrosion of iron and steel and is often used as a corrosion inhibitor in open and closed recirculating cooling water systems [23–26].

The primary nitrogen species considered in this survey are: NO_3^-, NO_2^-, NO, $N_2O_3^{2-}$, NO^-, RNO, nitrenes ($R_2N=N$, RN), N^{3-}, N_3^-, RNH_2 and NH_3. There are a few iron complexes with each of the species except for NO, where there are many. The iron–nitrosyl complexes have been surveyed in a number of recent reviews [27–31]. Probably the most studied of these complexes are $[Fe(CN)_5NO]^{2-}$, $FeNO^{2+}$(aq), and [PorFeNO]. No iron complexes of N_2, NH_2OH, and N_2H_4 have been found. Much of this review deals with the reactivity of the nitrogen species bound to iron or the role that iron has in promoting the reaction of the nitrogen species.

In most cases one, or possibly two, nitrogen species in the initial reaction stages bind to an iron(II) or (III) center which has other ligands attached to complete the five- or six-coordinate environment. There appear to be six primary coordination environments that are employed by iron in its interaction with nitrogen species (X): (a) $[Fe(H_2O)_5X]^{n+}$ in aqueous solutions; (b) $[Fe(CN)_5X]^{n+}$; (c) $[Fe(A)X]^{n-}$ where A is a polyaminocarboxylic acid anion such as $edta^{4-}$; (d) [PorFeX] where Por is a porphyrin anion; (e) $[Fe(NO)_xL_y]$ where L is usually a unidentate ligand; and (f) $[Fe(L)_xX]$ where L is a multidentate ligand. Each of these environments interacts with certain nitrogen species better than with others, or at least more is known about these interactions than others. There are major gaps in our knowledge of this chemistry and hopefully this review will point out these gaps.

There is a large volume of literature treating this area of chemistry, especially since some of the chemistry was studied over a century ago. Much of the older literature is not covered since it serves as pertinent historical references in the more recent work being discussed. The literature through 1990 is surveyed.

B. NITRATE COMPLEXES AND REACTIONS

(i) Complexes

Twenty-one iron nitrate complexes are shown in Table 1. The majority of these are iron(III) complexes, formed by relatively simple substitution reactions. One useful preparative reaction is between iron μ-oxo complexes and acids [32]

$$[(LFe)_2O] + 2HNO_3 \rightarrow 2[LFeNO_3] + H_2O \tag{1}$$

Several nitrate complexes have been prepared in this way [33–34].

Nitrate may coordinate to metal ions in either a bidentate or unidentate

TABLE 1

Iron nitrate complexes

Compound	Mode[a]	X-ray?	Ref.
$[Ph_4As][Fe(NO_3)_4]$	B	Yes	38–40
$[Fe(NO_3)Cl_2(HMPA)_2]$	B	Yes	46
$[Fe(NO_3)_2Cl(OPPh_3)_2]$	B	Yes	45
$[TPPFe(NO_3)]$	B	Yes	33
$[CpFe(NO_3)(CO)_2]$	M	Yes	163
$[(BMEA)Fe(NO_3)_2]\cdot DMF$	B	Yes	164
$[salenFe(NO_3)]_2$	M	Yes	165, 166
$[acacenFe(NO_3)]$	B	Yes	167
$[salenFe(NO_3)]$	B	No	34
$[salphenFe(NO_3)]_2$	M	No	166
$[salmedienFe(NO_3)]$	M	No	168
$[saldienFe(NO_3)]$	M	No	168
$[TMLFe(NO_3)]$	M	No	169
$[iahFe(NO_3)_2]NO_3\cdot H_2O$	M, B	No	170
$[(HMBM\text{-}H)_2FeNO_3]\cdot 3H_2O$	B	No	171
$[(AMBM)(OH)(NO_3)_2]\cdot H_2O$	B	No	171
$[(HMBT\text{-}H)Fe(NO_3)_2]\cdot 2H_2O$	M	No	170
$[(N\text{-}bipyO)_2Fe(NO_3)_2]NO_3$	M	No	172
$[(N\text{-}phenO)_2FeNO_3](NO_3)_2$	B	No	172
$[(1\text{-}FIQTSC)Fe(NO_3)_2]$	M?[b]	No	173
$[(2\text{-}FQTSC)Fe(NO_3)_2]$	M?	No	173

[a] B = bidentate; M = monodentate.

[b] No mention of nitrate coordination mode was made, but the nature of the other ligands and the geometry of the complex indicates nitrate to have a monodentate coordination.

manner. Addison et al. [35] have established a criterion for classifying coordination modes based on the difference in the bond distances to the metal of the two nitrate oxygen atoms closest to the metal. If the difference is 0–0.2 Å, the coordination is symmetrical bidentate, while if the difference is greater than 0.8–1.1 Å, the coordination is unidentate. With a difference between 0.2 and 0.8 Å, the nitrate is bound in an unsymmetrical bidentate manner. Table 1 presents iron complexes with both uni- and bidentate nitrates, eight being established by crystal structure determination.

Nitrate coordination in the solid is often proposed on the basis of conductivity experiments, which show that little or no ionization occurs when the complex is dissolved in a non-polar solvent. It is assumed that the same coordination is maintained both in solution and the solid. The coordination mode is then determined by IR and Raman spectral measurements on the solid. There are many factors that determine the coordination mode, one of which is the way that the solid is precipitated from solution. The salenFe^+ group is able to bind nitrate in a uni- or bidentate manner in the solid state, depending on the organic solvent used to precipitate the nitrate complex from dichloromethane solution [34]. With pentane, dimers which have unidentate nitrates bound to each Fe atom, $[\text{salenFeONO}_2]_2$, precipitate, while monomers with bidentate nitrate ligands, $[\text{salenFeO}_2\text{NO}]$, precipitate when ether is used.

In water or other good coordinating solvents, the weakly bound nitrate is expected to be displaced from the metal. However, in water, Fe^{3+} can weakly bind nitrate. The formation constant of $Fe(NO_3)^{2+}$ is equal to $0.32\ M^{-1}$ at 25°C and an ionic strength of 1.0 [36].

(ii) Iron(III) nitrate complexes from nitrogen(IV) oxides

When N_2O_4 reacts with either $Fe(CO)_5$, $FeCl_2$ or $FeCl_3$, $NO^+[Fe(NO_3)_4]^-$ is produced. The sublimation of this compound gives $NO_2^+[Fe(NO_3)_4]^-$ [37]. Crystals of $R_4N^+[Fe(NO_3)_4]^-$ form according to the reaction [38]

$$R_4NCl + FeCl_3 + 4N_2O_4 \xrightarrow[\text{EtOAc}]{20^\circ\text{C}} R_4N^+[Fe(NO_3)_4]^- + 4NOCl \tag{2}$$

An examination of the crystals showed that each nitrate ligand in the anion is bound in a symmetrical bidentate manner to the iron, forming a flattened tetrahedral structure (Fig. 1) [39,40]. The eight O atoms lie at the corners of a trigonal dodecahedron. The reaction of excess N_2O_4 with $NO^+[Fe(NO_3)_4]^-$ gives $[N_4O_6][Fe(NO_3)_4]_2$ where the cation is made up of $3NO^+$ and a NO_3^- in a weakly associated group [38].

If a reaction of NO_2 and $Fe(CO)_5$ gases is carried out, a yellow-brown ferromagnetic powder, $FeO(NO_3)$, results [39]. This also forms as a coating on the anode when $R_4N^+[Fe(NO_3)_4]^-$ undergoes electrochemical oxidation in nitrobenzene [40].

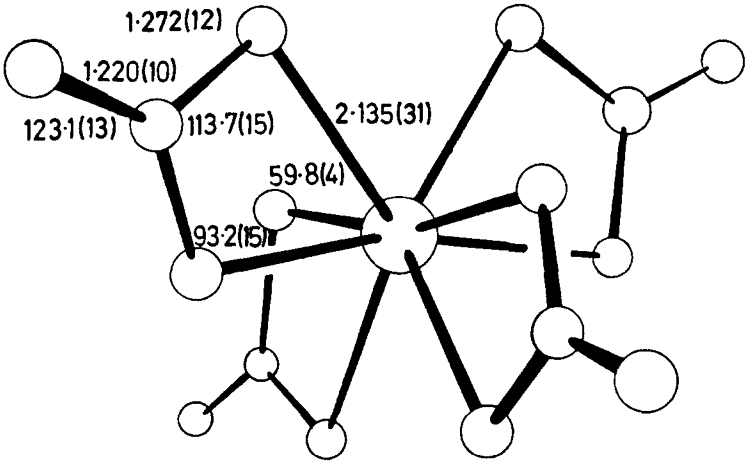


Fig. 1. Structure of the tetranitratoferrate(III) anion, $[Fe(NO_3)_4]^-$, indicating average bond lengths (in Å) and angles (in degrees) for the FeO_2NO unit. (Reproduced with permission from ref. 40.)

(iii) Reaction of nitrate and $Fe^{2+}(aq)$

This reaction in acid solution which forms the 'brown ring' has been of interest to chemists for decades. Epstein et al. [41] have made a detailed kinetics study of the reaction under batch conditions and in a continuous flow stirred tank reactor [42]. The overall reaction is:

$$3Fe^{2+} + 4H^+ + NO_3^- \rightarrow 3Fe^{3+} + 2H_2O + NO \tag{3}$$

Reaction (3) can be monitored by measuring either the absorbance of the $FeNO^{2+}$ intermediate as it is formed or the potential of the Fe(III)/Fe(II) couple. It is one of several examples of autocatalytic nitric acid oxidation reactions [43]. The reaction scheme is complex with at least seven principal reactions ((4)–(10)), four of which involve Fe^{2+} reacting with oxynitrogen species:

$$Fe^{2+} + NO_3^- + 2H^+ \rightleftharpoons Fe^{3+} + H_2O + NO_2 \tag{4}$$

$$Fe^{2+} + NO_2 + H^+ \rightleftharpoons Fe^{3+} + HNO_2 \tag{5}$$

$$Fe^{2+} + HNO_2 + H^+ \rightleftharpoons Fe^{3+} + NO + H_2O \tag{6}$$

$$Fe^{2+} + NO \rightleftharpoons FeNO^{2+} \tag{7}$$

$$2NO_2 + H_2O \rightleftharpoons HNO_2 + NO_3^- + H^+ \tag{8}$$

$$2HNO_2 \rightleftharpoons NO + NO_2 + H_2O \tag{9}$$

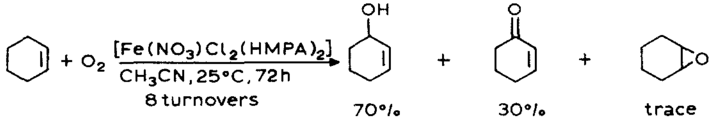
$$NO + NO_3^- + H^+ \rightleftharpoons NO_2 + HNO_2 \tag{10}$$

The rate-determining step is reaction (10).

In basic solution, Fe^{2+} and NO_3^- produce ammonia in nearly quantitative yield with no formation of nitrogen, but at a much slower rate than the reaction of Fe^{2+} and NO_2^- (Sect. D(i)) [44]. However, silver(I) catalyzes the NO_3^- reduction. Ammonia is also produced under the same conditions by the reduction of hydroxylamine with Fe^{2+}.

(iv) O_2 activation

The activation of dioxygen is possible using the chloro or iodo nitrosyl complex, $[Fe(NO)_2X]_2$ [45–47]. These compounds react readily with O_2 in the presence of a phosphorus base (L) to form nitrato complexes such as $[Fe(NO_3)X_2L_2]$ or $[Fe(NO_3)_2XL_2]$, and they can serve as catalysts for the oxidation of PPh_3 or cyclohexene [46]. One example is:



(11)

The catalysts have symmetrical bidentate nitrate groups bound to the Fe atom. The structure of $[Fe(NO_3)_2Cl(OPPh_3)_2]$, a catalyst for PPh_3 oxidation, has a seven-coordinate pentagonal bipyramidal structure with two symmetrically bound bidentate nitrates, but with chelate rings of different size (Fig. 2) [45]. The bond distances of one of the four-membered chelate rings is: N–O, 1.074, 0.985 Å and Fe–O, 2.099,

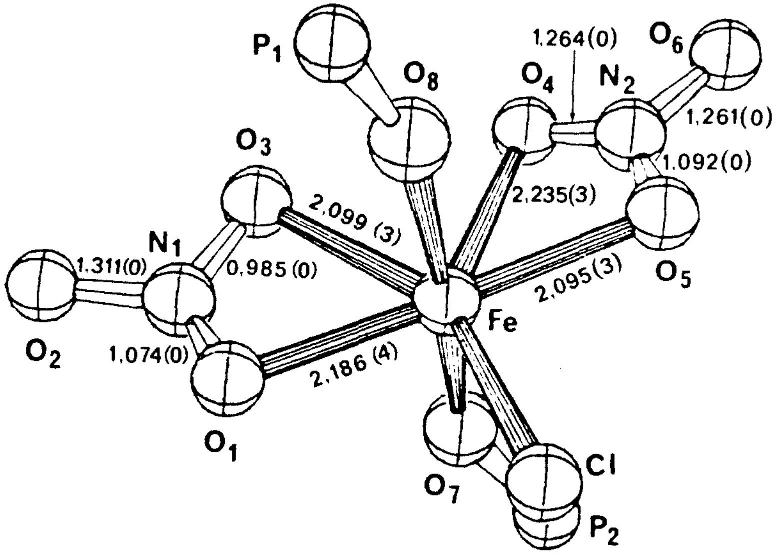


Fig. 2. Structure of $[Fe(NO_3)_2Cl(OPPh_3)_2]$. (Reproduced with permission from ref. 45.)

2.186 Å; the other has: N–O, 1.092, 1.264 Å and Fe–O, 2.095, 2.235 Å. Thus, one ring is more asymmetric than the other.

C. NITRITE COMPLEXES

(i) Iron(II) complexes

The interaction of nitrite with iron(II) is governed primarily by the redox potentials of the species involved. For example, reaction (12) has an E^0 value at 25°C of 0.212 V [48].

$$Fe^{2+}(aq) + HNO_2(aq) + H^+(aq) \rightarrow NO(g) + Fe^{3+}(aq) + H_2O \qquad (12)$$

Few iron–nitrite complexes have been reported, and only two, $[Fe(NO_2)_6]^{4-}$ and $[Fe(CN)_5NO_2]^{4-}$, were mentioned in an extensive review of metal nitrite complexes [49]. The hexanitro complex has been studied in the solid state as $K_2M^{II}[Fe(NO_2)_6]$, where M is Ba or Pb [50]. These compounds are prepared by reacting solutions of $Fe(NO_3)_2$, $M(NO_2)_2$, and $NaNO_2$ with sodium acetate added to prevent NO formation. The solid state electronic spectra [51,52] and Mössbauer spectra [53,54] of the iron(II) hexanitro compounds have been described. Ferrari et al. [55,56] reported several $[Fe(NO_2)_6]^{4-}$ compounds which were prepared by keeping the iron(II) concentration low and NO_2^- concentration high in order to minimize redox reactions. Even then, some of the compounds had low iron and nitrite analyses.

The cyano complex, $[Fe(CN)_5NO_2]^{4-}$, in solution is in equilibrium with the nitrosyl complex [57,58]:

$$[Fe(CN)_5NO_2]^{4-} + 2H^+ \rightleftharpoons [Fe(CN)_5NO]^{2-} + H_2O \qquad (13)$$

The conversion to the nitrosyl can also be carried out in the solid state by photolysis [59]. In solution at high pH, the O atoms of the nitro group exchange with the O atoms of water [60]. Considerable attention has been given to the nitrosyl complex, for it has been treated in a number of reviews dealing with transition metal cyanide and nitrosyl complexes [27,29–31,61]. Some aspects of this chemistry are discussed below and in other sections of this report.

It was surprising to find two iron(II) nitrite complexes that were prepared in a relatively simple manner, especially since there is an extensive literature covering the reactions of iron(II) complexes with nitrite (Sect. D). The macrocyclic complexes, $[Fe[14]aneN_4(NO_2)_2]$, $[Fe[15]aneN_4(NO_2)]^+PF_6^-$, and $[\{Fe[16]aneN_4(NO_2)\}_2NO_2]^+PF_6^-$, were prepared by mixing an alcoholic solution of an alkali metal nitrite with a CH_3CN solution of the $[Fe[n]aneN_4]^{2+}$ complex, where $[n]aneN_4$ represents the tetradentate, neutral N_4 macrocyclic ligands with a 14-, 15-, or 16-membered chelate ring [62]. The three complexes have formulas based on IR spectra and conductivity measurements, and each has a different magnetic nature and Mössbauer spectrum. The Mössbauer spectra at several temperatures of the low-spin complex,

$[Fe(phen)_2(NO_2)_2]$, prepared by stirring $[Fe(phen)_3](NO_2)_2 \cdot 7H_2O$ in cold, absolute acetone, have been reported [63]. The reactivity of these complexes with acid has not been examined to determine if they behave in a manner similar to that of $[Fe(CN)_5NO_2]^{4-}$.

(ii) Iron(III) complexes

There are very few iron(III) nitrite complexes. In aqueous solution, a complex $Fe(NO_2)^{2+}$ is reported to have a formation constant of 740 M^{-1} at 25°C and an ionic strength of 0.01 M [64]. The measurements were made with 0.01 M $HClO_4$ present, yet no mention was made of any HNO_2 disproportionation to NO and NO_3^-, which is expected to take place under these conditions considering E^0 values [48]. $K_3[Fe(CN)_5NO_2]$ has been prepared by reacting $KMnO_4$ with $Na_2[Fe(CN)_5NO]$ under basic conditions [65,66]. The complex ion is stable in aqueous solution only in the pH range of 5–10. In acid solution, it hydrolyzes by the mechanism [67]:

$$[Fe(CN)_5NO_2]^{3-} + H^+ \rightleftharpoons [Fe(CN)_5NO_2H]^{2-} \qquad \text{fast, equilibrium, } K_{14} \tag{14}$$

$$[Fe(CN)_5NO_2H]^{2-} + H^+ \rightarrow [Fe(CN)_5NO]^- + H_2O \qquad \text{slow, } k_{15} \tag{15}$$

$$[Fe(CN)_5NO]^- + H_2O \rightarrow [Fe(CN)_5H_2O]^{2-} + NO^+ \qquad \text{slow} \tag{16}$$

The observed k $(=k_{15}K_{14}[H^+]^2/(1+[H^+]))$ increases with a decrease in pH. Base hydrolysis is catalyzed by an electron transfer path involving trace amounts of $[Fe(CN)_5NO_2]^{4-}$ that are present. Solvolysis of $[Fe(CN)_5NO_2]^{3-}$ in DMF, DMSO, and CH_3OH occurs by a limiting dissociative mechanism and is much faster in these solvents than in water [68].

The iron(III) porphyrin nitrite complex, $[K(18\text{-}C\text{-}6)(H_2O)]^+[Fe(TpivP)(NO_2)_2]^-$, has been prepared and the structure determined as part of an examination of the reaction of NO_2^- with iron(III) porphyrins [69]. The structure is discussed in Sect. D(iii). Mono- and bis-nitrite complexes have been proposed to form when $TPPFe^+$ reacts with nitrite in DMF [70]. However, the stability of these complexes has been questioned (Sect. D(iii)) [71].

The NO_2^- ion can bind to a metal ion in a variety of ways [49]. All of the iron(II) and (III) complexes appear to be of the nitro type with the NO_2^- bound to the Fe atom through the N atom, except for $[\{Fe[16]aneN_4(NO_2)\}_2NO_2]^+PF_6^-$ where one of the NO_2^- ligands is bridging the two Fe atoms [62].

D. NITRITE REACTIONS

Below is given a survey of the reactions of nitrite, most of which take place in acidic or basic aqueous solution. In many cases, the oxidation of iron(II) by nitrite occurs to form the nitrosyl complex and iron(III) (reaction (23)). However, as discussed below, nitrite can serve as a reducing agent for iron(III) complexes. It is not possible to separate the chemistry of iron–nitrite systems from that of the iron–nitrosyl systems. Discussion of the iron–nitrosyl complexes is given in Sect. E, even though it is necessary that some of its features are treated here.

Reactions of NO_2^- with iron complexes are difficult to study, especially in highly acidic solutions, since many oxynitrogen species may be present and be kinetically active. Most form in rapidly established equilibria:

$$H^+ + NO_2^- \rightleftharpoons HNO_2 \tag{17}$$

$$H^+ + HNO_2 \rightleftharpoons H_2NO_2^+ \text{ (or } H_2O + NO^+) \tag{18}$$

$$2HNO_2 \rightleftharpoons N_2O_3 + H_2O \tag{19}$$

$$N_2O_3 \rightleftharpoons NO + NO_2 \tag{20}$$

$$2NO_2 \rightleftharpoons N_2O_4 \tag{21}$$

$$N_2O_4 + H_2O \rightleftharpoons HNO_2 + H^+ + NO_3^- \tag{22}$$

Great care must be taken in carrying out such studies in order to determine the proper reactant species.

(i) $Fe^{2+}(aq)$

The reaction in acid solution with a low concentration of reactants and a high Fe^{2+}/nitrite ratio rapidly produces the brown $FeNO^{2+}$ complex:

$$2Fe^{2+} + HNO_2 + H^+ \rightarrow FeNO^{2+} + Fe^{3+} + H_2O \tag{23}$$

At high reactant concentrations and a Fe^{2+}/HNO_2 ratio of 1, the reaction is used for the laboratory preparation of NO [72]. Many workers have studied the reaction forming $FeNO^{2+}$, and their work has been surveyed and the reaction examined in some detail [73]. At a pH of 3 or less, only the exceptionally stable $FeNO^{2+}$ ion is formed. Increasing the pH to 6 with a ratio of iron(II) to NO_2^- of 2 gives 84% N_2O. If the pH goes over 8, N_2 becomes a product.

Using stopped-flow kinetics, the rate law for the oxidation of $Fe(H_2O)_6^{2+}$ in the pH range 0.90–3.1 at 25°C and 0.5 M ionic strength was found to be [14]:

$$\text{Rate} = (174 \pm 23\ M^{-2}\,s^{-1})[HNO_2]^2[Fe(II)]$$

The following mechanism was postulated:

$$HONO + HONO \rightleftharpoons N_2O_3 + H_2O \qquad \text{equilibrium} \tag{24}$$

$$Fe(II) + N_2O_3 \rightarrow Fe(III) + NO + NO_2^- \qquad \text{slow} \tag{25}$$

$$Fe(II) + NO \rightarrow FeNO^{2+} \qquad \text{fast} \tag{26}$$

To carry out this study it was necessary to keep the pH <3.2 in order to prevent formation of hydroxo species. Going to pH 4 and above produces a sequential reduction of NO_2^- with NO first forming and then N_2O [73]. At pH 6 and an initial ratio of NO to iron(II) of 2, 99% N_2O is produced. Using added $N_2O_3^{2-}$ and nitrogen labelling, Fe^{2+} was shown to reduce NO to HNO, which leads to N_2O:

$$Fe^{2+} + NO + H^+ \rightarrow Fe^{3+} + HNO \tag{27}$$

$$2HNO \rightarrow N_2O + H_2O \tag{28}$$

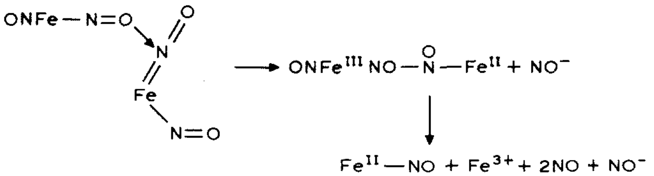
The rate of the reaction

$$2H^+ + Fe(II) + 2NO \rightarrow 2Fe(III) + N_2O + H_2O \tag{29}$$

was followed at pH 6 and 25°C in a concentrated (2.0 M) acetate solution, thereby promoting dinitrosylcomplex formation (Sect. F(i)). The following rate expression was determined [74]:

$$\text{Rate} = (1.6 \pm 0.4) \times 10^{-4}\ s^{-1}[Fe(NO)_2^{2+}] + (4.7 \pm 0.2) \times 10^{-2}\ M^{-1}\ s^{-1}[Fe(NO)_2^{2+}]^2$$

The mechanism for the second-order term was proposed to be:



(30)

Not much could be said about the first-order low-stoichiometric-ratio pathway.

The reaction of NO_2^- with iron(II) in NaOH solutions leads to the formation of NH_3 [44]. Also, solutions of NO_3^- and NH_2OH solutions produce NH_3 with iron(II) under the same conditions (Sect. B(iii)). No nitrogen or gaseous oxides were observed. The rates of reaction were $NO_2^- > NH_2OH \gg NO_3^-$. It was speculated that the reduction below nitrogen(I) may be due to the presence of an iron hydroxide gel.

(ii) $Fe^{II}(edta)(aq)$

The reaction of the edta complex and polyaminocarboxylate (A) complexes with nitrite over the pH range 2–5 is [14,15]:

$$H^+ + 2Fe^{II}A + HNO_2 \rightarrow Fe^{III}A + Fe^{II}A(NO) + H_2O \tag{31}$$

The reaction is slightly slower than that for Fe^{2+}(aq) and rate measurements found the rate law for the edta complex to be:

$$\text{Rate} = (62 \pm 12)\ M^{-1}\ s^{-1}[HNO_2]^2 + (90 \pm 16)\ M^{-1}\ s^{-1}[Fe^{II}(edta)][HNO_2]$$

at 25°C and 0.5 M ionic strength. The mechanism proposed for the reaction is:

(1st term)

$$HONO + HONO \rightarrow N_2O_3 + H_2O \qquad \text{slow, } k_{32} \tag{32}$$

$$Fe^{II}A + N_2O_3 \rightarrow Fe^{III}A + NO + NO_2^- \qquad \text{fast} \tag{33}$$

$$Fe^{II}A + NO \rightarrow Fe^{II}A(NO) \qquad \text{fast} \tag{34}$$

(2nd term)

$$HONO + Fe^{II}A \rightarrow Fe^{III}A + NO + OH^- \qquad \text{slow, } k_{35} \tag{35}$$

$$Fe^{II}A + NO \rightarrow Fe^{II}A(NO) \qquad \text{fast} \tag{36}$$

In terms of the mechanism

$$\text{Rate} = 2k_{32}[HNO_2]^2 + 2k_{35}[Fe^{II}A][HNO_2]$$

The contribution of each path depends on the nature of the polyaminocarboxylate ligand, pH, and total $[NO_2^-]$. The nitrogen(III) species that oxidizes $Fe^{II}A$ according to the first-term mechanism (reactions (32)–(34)) might be NO^+ rather than N_2O_3, as it is in the acid solution reaction of Fe^{2+}(aq) and NO_2^- (reactions (24)–(26)). The first-term mechanism is very similar to that for the Fe^{2+}/NO_2^- reaction except that the relative rates for the first two steps are reversed. Compare reaction (24) with reaction (32) and reaction (25) with reaction (33). The lack of a direct reaction between HNO_2 and Fe^{2+} is due to the high redox potential for Fe^{3+}/Fe^{2+}.

(iii) Iron(III) porphyrin and Schiff base complexes

The reaction of iron(III) porphyrins and nitrite usually leads to the formation of [PorFeNO], but if the *meso* position of the ligand is not protected, *meso*-nitration may occur [75]. OEPFeCl dissolved in THF and shaken with an acidified $NaNO_2$ solution results in the rapid formation of OEPFeNO. However, if the reaction is carried out with the OEPFeCl dissolved in $CHCl_3$ and a mixture of acetic acid and $NaNO_2$ is added under nitrogen, the porphyrin reacts to form [(5-nitro-OEP)FeCl].

In CH_2Cl_2, the reaction of $TPPFe^+$ complexes with soluble nitrite salts rapidly leads to the formation of [TPPFeNO] and NO_3^- [71]. In DMF, it appears that the $TPPFe^+$/nitrite system is much more unstable than reported [70]. Upon mixing the reactants in DMF, a highly reactive intermediate forms which is proposed to be a bis-nitrite complex of some undefined structure, possibly a nitro-nitrito complex, $[TPPFe(NO_2)(ONO)]^-$. This complex reacts with nitrite within minutes to form $[TPPFe(NO)(ONO)]^-$ and NO_3^-. The nitrosyl-nitrito product has moderate stability in solution; however, it could not be isolated. The kinetics of the reaction forming the final product from the intermediate were examined and the following rate law was found:

$$\text{Rate} = k[\text{Intermediate}][NO_2^-]$$

The proposed mechanism involves a single O atom transfer from the coordinated nitrite to the uncoordinated nitrite:

$$TPPFeX + 2NO_2^- \rightarrow [TPPFe(NO_2)_2]^- + X^- \tag{37}$$

$$[TPPFe(NO_2)_2]^- + NO_2^- \rightarrow [TPPFe(NO)(ONO)]^- + NO_3^- \tag{38}$$

where $X = Cl^-$, ClO_4^- or NO_3^-.

A low-spin bis(nitro) iron(III) picket-fence porphyrin complex, $[K(18\text{-}C\text{-}6)(H_2O)]^+[(TpivPP)Fe(NO_2)_2]^-$, was isolated by reacting the iron(III) porphyrin in chlorobenzene with KNO_2 solubilized using 18-crown-6 [69]. Crystals of the bis-nitro complex were formed and the structure determined (Fig. 3). The two nitrite ions are coordinated to the Fe atom through N atoms above and below the porphyrin plane. The NO_2 group outside the porphyrin 'pocket' was coordinated to the K^+ through the O atoms of the nitrite. Solutions of the complex in CH_2Cl_2 were used to determine the stepwise formation constants for nitrite complexation (K_1, 1.49×10^4 M^{-1}; K_2, 4.0×10^4 M^{-1}). Ion-pair formation with the cation enabled the bis complex to have significant stability in solution.

The reaction of $[Fe(salen)NO_3]$ and $[Fe(salen)Cl]$ with $[(PPh_3)_2N]^+NO_2^-$ in acetonitrile rapidly produces the μ-oxo complex, NO and NO_3^- [76]:

$$2[Fe(salen)]^+ + 3NO_2^- \rightarrow [Fe(salen)]_2O + 2NO + 3NO_3^- \tag{39}$$

The stoichiometry has been determined by carrying out the reaction on a vacuum line in order to measure the amount of NO evolved and measuring the amount of NO_3^- produced with ion chromatography. Stopped-flow studies show that the reaction appears to go through a $[Fe^{III,IV}(salen)]_2O^+$ intermediate. The related Schiff base complex, [Fe(acacen)Cl], does not yield NO and studies are under way to determine the nature of the products.

(iv) $Fe[TMP]_3^{3+/2+}$ couple

The reaction of the $[Fe(TMP)_3]^{3+/2+}$ (TMP = 3,4,7,8-tetramethylphenanthroline) redox couple in nitrous acid solutions was examined since the couple has an oxidation potential within 0.04 V of the $[Fe(H_2O)_6]^{3+/2+}$ couple [77,78]. The kinetic effects of complexation on the iron–nitrite reactions were determined, and very different reactivities found.

At low acidity, the +3 complex is reduced quantitatively:

$$2[Fe(TMP)_3]^{3+} + NO_2^- + H_2O \rightarrow 2[Fe(TMP)_3]^{2+} + NO_3^- + 2H^+ \tag{40}$$

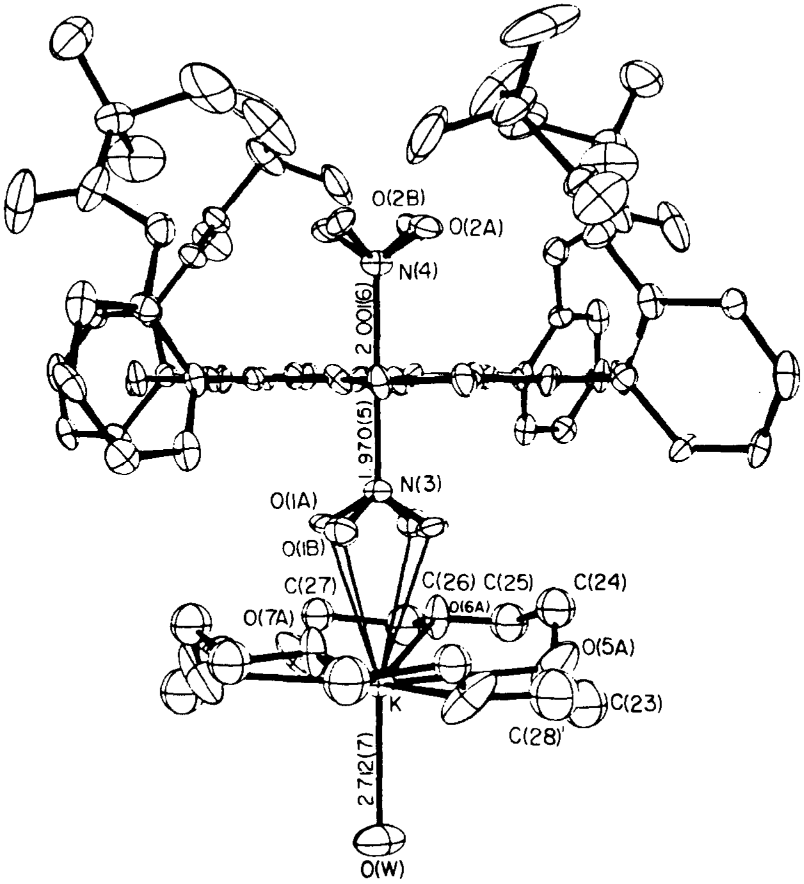


Fig. 3. Structure of $[K(18\text{-}C\text{-}6)(H_2O)][Fe(NO_2)_2(TpivPP)]$, showing closest approach of $[K(18\text{-}C\text{-}6)(H_2O)]^+$ to the exposed nitrite. Both orientations of the two disordered nitrite ions are shown. (Reproduced with permission from ref. 69.)

while at high acidity, the +2 complex is oxidized quantitatively:

$$[Fe(TMP)_3]^{2+} + HNO_2 + H^+ \rightarrow [Fe(TMP)_3]^{3+} + NO + H_2O \tag{41}$$

Both reaction (40) and reaction (41) have been examined using stopped-flow kinetics. The low-acidity iron(III) reduction mechanism is proposed to be:

$$HNO_2 \rightleftharpoons H^+ + NO_2^- \tag{42}$$

$$[Fe(TMP)_3]^{3+} + NO_2^- \rightleftharpoons [Fe(TMP)_3]^{2+} + NO_2 \tag{43}$$

$$2NO_2 + H_2O \rightarrow HNO_2 + NO_3^- + H^+ \qquad \text{fast} \tag{44}$$

The rate law at 25.0° and 0.3 M ionic strength explained by the mechanism is:

$$\text{Rate} = (3.9 \pm 0.09) \times 10^3\ M^{-1}\ s^{-1}[N(III)]/(1 + [H^+]/(9.6 \pm 0.86) \times 10^{-4}\ M)$$

Biphasic kinetics were found in the high-acidity oxidation reaction, giving a rate law at 25.0°C and 1.0 M ionic strength of:

$$\text{Rate} = \{(9.54 \pm 0.85) \times 10^1\ \text{M}^{-1}\,\text{s}^{-1}[\text{HNO}_2] + (1.28 \pm 0.02) \times 10^{-4}\ \text{M}^{-2}\,\text{s}^{-1}[\text{HNO}_2]^2\}[\text{Fe(TMP)}_3^{2+}]$$

The addition of NO to the high-acidity reaction had a strong inhibiting effect on the reaction rate. The mechanism given below was proposed by Ram and Stanbury [77]:

$$2\text{HNO}_2 \rightleftharpoons \text{NO} + \text{NO}_2 + \text{H}_2\text{O} \quad (9)$$

$$2\text{NO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HNO}_2 + \text{NO}_3^- + \text{H}^+ \quad (45)$$

$$[\text{Fe(TMP)}_3]^{2+} + \text{NO}_2 \rightarrow [\text{Fe(TMP)}_3]^{3+} + \text{NO}_2^- \quad (46)$$

$$[\text{Fe(TMP)}_3]^{2+} + \text{HNO}_2 \rightarrow [\text{Fe(TMP)}_3]^{3+} + \text{HNO}_2^- \quad (47)$$

$$\text{H}^+ + \text{HNO}_2^- \rightarrow \text{NO} + \text{H}_2\text{O} \quad (48)$$

The first term of the rate law represents the direct reaction of the complex with HNO_2 (reaction (47)). The second term is strongly affected by NO and is dominated by the rapid equilibrium forming NO_2 and NO (reaction (9)); therefore, the second term considers the reaction of NO_2 with the +2 complex (reaction (46)).

The entire reaction sequence is illustrative of the potential that NO_2^- and the other oxynitrogen species involved have for outer-sphere electron transfer. The studies with the $[Fe(TMP)_3]^{3+/2+}$ couple show that the NO^+/NO couple does not play a role; rather it is more likely that it is the NO_2/NO_2^- couple which determines the pathway of these reactions.

It should be noted that oxidation of iron complexes to higher oxidation states can be achieved with $NO^+BF_4^-$ with no apparent oxynitrogen complex formation [79]. The use of this reagent with iron(III) complexes can produce iron(IV) complexes (see, for example, ref. 80).

(v) $[Fe(CN)_6]^{4-}$(aq)

The oxidation of this substitution inert complex by nitrite proceeds by an outer-sphere electron transfer path. However, reactions have been carried out from low (0.1 M) to high (6 M) nitrous acid concentrations in order to understand the preparation of the nitroprusside ion, $[Fe(CN)_5NO]^{2-}$, from $[Fe(CN)_6]^{4-}$ which occurs in 30% nitric acid [81,82]. In such a solution, nitrous acid is expected to be present, or it would result from the oxidation of $[Fe(CN)_6]^{4-}$ by nitrate. Other substitution inert complexes, such as $[Fe(L)_2(CN)_2]$ where L is bpy or phen, react in a similar manner [83]. The proposed oxidation mechanism involves NO^+ reacting with the iron(II) complex to produce NO and $[Fe(CN)_6]^{3-}$. An alternative mechanism for these acid solution reactions has been suggested and has NO_2 reacting with the iron(II) complex [77]:

$$2HNO_2 \rightleftharpoons NO_2 + NO + H_2O \qquad (9)$$

$$NO_2 + [Fe(CN)_6]^{4-} \rightarrow NO_2^- + [Fe(CN)_6]^{3-} \qquad (49)$$

Reaction (49) has been shown to occur in aqueous solution where NO_2 is formed by e_{aq}^- reacting with NO_3^- [84].

(vi) [Fe(CO)$_5$]

Iron carbonyl reactions with nitrite were carried out by Hieber and Beutner [85] to produce the $[Fe(CO)_3NO]^-$ ion. In methanol with methoxide added, nitrite reacts quantitatively with $Fe(CO)_5$:

$$[Fe(CO)_5] + NO_2^- + CH_3O^- \rightarrow [Fe(CO)_3NO]^- + CH_3OCO_2^- + CO \qquad (50)$$

The nitrosylation reaction has been studied in some detail using THF and CH_3CN as solvents and $(Ph_3P)_2N^+NO_2^-$, which dissolves in THF when $[Fe(CO)_5]$ is added [86]. The mechanism in aprotic solvents involves nucleophilic attack of the nitrite ion on one of the carbonyl C atoms and loss of CO to form a four-coordinate intermediate. The intermediate may rearrange to form the nitrosyl product and lose CO_2; or it may undergo attack by a second nitrite to produce the ultimate products.

(vii) [Fe$_2$(SR)$_2$(NO)$_4$]

Nitrite reacts with the esters (R = Me, Et, and Ph) to produce $[Fe(NO)_2(NO_2)_2]^-$, employing a general reaction found for a wide variety of nucleophilic anions(X) [87,88]:

$$[Fe_2(SR)_2(NO)_4] + 4X^- \rightarrow 2RS^- + 2[Fe(NO)_2X_2]^- \qquad (51)$$

The reaction with nitrite has been carried out in CH_2Cl_2, acetone and DMF and studied with ^{15}N NMR and ESR. Even though the paramagnetic $[Fe(NO)_2(NO_2)_2]^-$ anion has been described as extremely stable, it was not isolated from solution.

The reaction of iron–nitrosyl complexes with nitrite has shown the ability of the NO group to exchange with the nitrite through the 'W intermediate' [89,90]. This is discussed in Sect. G(iv), which deals with N_2O_3 reactions.

E. THE ELECTROCHEMISTRY OF IRON-NITRITE/NITROSYL SYSTEMS

The electrochemical studies discussed in this section involve the electrochemical reduction of nitrosyl complexes that are formed either by the addition of acid to a nitrite solution in the presence of the iron complex or by the addition of NO to the solution of the complex. The reduction is then carried out in more than 1 e$^-$ steps to produce N_2O, NH_2OH, N_2H_4, and/or NH_3. Electrochemical reductions are described in other sections of this report, but the ones discussed here consider the potential for the iron complex to serve as a catalyst for the production of NH_3 from NO_2^-.

(i) Iron porphyrins

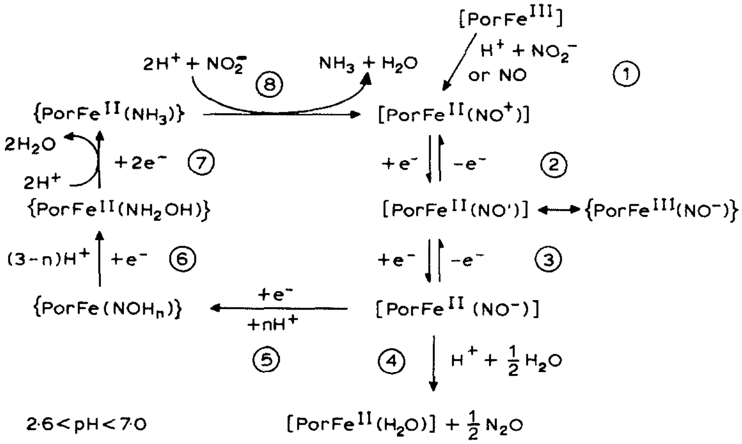
The water-soluble iron porphyrin complexes, Fe^{III}(TPPS) and Fe^{III}(TMpyP) (where TPPS is the tetraanionic *meso*-tetrakis(*p*-sulfonatophenyl)porphyrin and TMpyP is *meso*-tetrakis(*N*-methyl-4-pyridyl)porphine dication) were dissolved at millimolar concentrations in pH 4.5 and 6.7 buffer solutions with an excess of nitrite ($[NO_2^-]/[Fe]$ ranging from 20 to 300) present [91,92]. The solutions were subjected to electrolytic reduction at -0.9 V (FeTPPS) and -0.65 V (FeTMpyP) for several hours. Over this period, NH_3, NH_2OH, and a small amount of N_2O formed, but no N_2. To explain this catalyzed electrochemical reduction of nitrite, Scheme 1 has been developed based on detailed electrochemical experiments.

Step 1 of Scheme 1 involves the initial formation of the electroactive species, $[PorFe^{II}(NO^+)]$. The addition of NO_2^- to the Fe^{III}Por solution shows no indication of nitrite complex formation; however, if the solution is acidic enough, $[PorFe^{II}(NO^+)]$ forms. The nitrosyl complex may form by the direct addition of $NO_{(g)}$ into the solution:

$$3HNO_2 \rightleftharpoons 2NO + NO_3^- + H_2O + H^+ \qquad (52)$$

$$PorFe^{III} + NO \rightarrow [PorFe^{II}(NO^+)] \qquad (53)$$

Step 2 of Scheme 1 shows the 1 e^- reduction of $PorFe^{II}(NO^+)$. The reduction is a pH-independent, kinetically slow process that occurs at $+0.35$ V (TPPS) and



Scheme 1.

+0.55 V (TMpyP) vs. SCE. The next 1 e^- reduction (step 3) takes place at −0.64 V (TPPS) and −0.57 V (TMpyP) forming [$PorFe^{II}(NO^-)$]. Under certain conditions of pH and applied potential, some nitrogen is lost from the catalytic reduction as N_2O. The mechanism of N–N coupling to form N_2O is not known, but it is of interest that N–N coupling occurs at the 2 e^- stage, but not at the 3 e^- stage to form N_2 or the 5 e^- stage to form N_2H_4. Up to, and including, step 3 in Scheme 1, the reduction steps could be analyzed individually in some detail, and the species are shown in brackets. Those species shown in braces are intermediates whose presence is inferred without experimental evidence, or they represent an alternate electronic form of the species. The inferences are based primarily on the chemistry of ruthenium and osmium polypyridyl complexes [93,94]. Steps 5 and 6 account for the production of NH_2OH. Step 7 completes the cycle with the displacement of NH_3 by NO.

(ii) Fe(edta)

Nitrite solutions of pH 3–6 containing Fe^{II}(edta) have undergone electrochemical reduction at −1.3 V and an apparent electron number (n_{app}) of 3 was found [95]. This was explained by the formation of NH_2OH:

$$Fe^{II}(edta)(NO) + 3H^+ + 3e^- \rightarrow Fe^{II}(edta) + NH_2OH \tag{54}$$

Solutions of a similar nature, but with Fe^{II}(nta) replacing the edta complex, had a n_{app} value of 3 below pH 4, while above pH 5, the n_{app} value was 4. Between pH 4 and 5, non-integral values of n_{app} between 3 and 4 were found. Such values would occur if NH_2OH formed below pH 4 and N_2H_4 above pH 5, and a mixture of the two between pH 4 and 5. N_2O was not observed in these experiments.

Nitric oxide was bubbled into a solution of Fe^{II}(edta) at pH 6, and NH_3, NH_2OH, and N_2H_4 were formed by electrolysis at constant potential over the range of −0.4 to −1.8 V [96]. Only a negligible amount of N_2O was observed. The efficiency of conversion of NO to NH_3 by the Fe^{II}(edta) complex was compared with that of the Fe^{2+}(aq), Fe^{II}–py, and Fe^{II}–phen solutions. This comparison showed that, in order for a complex to have a high conversion efficiency, it must have moderate stability and not too many ligand sites blocked by the chelate.

Electrochemical reduction was carried out on a pH 5 nitrite solution containing Fe^{II}(edta) at a nitrite-to-iron ratio of 20 and at an applied potential of −0.90 V [97]. The products of the electrolysis were a mixture of NH_3, NH_2OH, N_2, and N_2O, all in reasonable amounts. Carrying out a similar experiment with Fe^{2+}(aq), except at pH 2.1, showed N_2O as the major product with smaller amounts of N_2 and NH_3 and no NH_2OH.

(iii) Iron-substituted polyoxotungstate

Four highly stable iron-substituted heteropolytungstates, $[H_2OFe^{III}XW_{11}O_{39}]^{n-}$ (X = Si or Ge, $n = 5$; X = As or P, $n = 4$) were prepared and their electrochemical nature in aqueous solution established [98]. The addition of NO_2^- to solutions of the iron(III) species showed no indication of any interaction since no visible spectral change occurred. A controlled potential reduction of the solution gave the iron(II) species which reacted with the nitrite to form the NO complex. Coulometry at the reduction potential of −0.4 V for the Si complex indicated the following reaction sequence:

$$2[H_2OFe^{III}SiW_{11}O_{39}]^{5-} + 2e^- \rightarrow 2[H_2OFe^{II}SiW_{11}O_{39}]^{6-} \qquad (55)$$

$$2[H_2OFe^{II}SiW_{11}O_{39}]^{6-} + HNO_2 \rightarrow [ONFe^{II}SiW_{11}O_{39}]^{6-} + [H_2OFe^{III}SiW_{11}O_{39}]^{5-} + 2H_2O \qquad (56)$$

The nitrosyl complex could also be prepared by bubbling NO into a solution of the iron(II) complex. The kinetics of the reaction of the four iron(II) complexes with nitrite was established and found to have a second-order rate constant that was pH-dependent from pH 3.3 (the pK_a of HNO_2 is 3.3) to pH 8, showing that the reactive form of the nitrite was HONO. These experiments led to the following scheme for the formation of the NO complex:

$$NO_2^- + H^+ \rightleftharpoons HNO_2 \qquad (57)$$

$$HNO_2 + [H_2OFe^{II}XW_{11}O_{39}]^{(n+1)-} \rightleftharpoons [HONOFe^{II}XW_{11}O_{39}]^{(n+1)-} + H_2O \qquad (58)$$

$$[HONOFe^{II}XW_{11}O_{39}]^{(n+1)-} \rightarrow [HOFe^{III}XW_{11}O_{39}]^{(n+1)-} + NO \qquad (59)$$

$$[H_2OFe^{II}XW_{11}O_{39}]^{(n+1)-} + NO \rightleftharpoons [ONFe^{II}XW_{11}O_{39}]^{(n+1)-} + H_2O \qquad (60)$$

$$[HOFe^{III}XW_{11}O_{39}]^{(n+1)-} + H^+ \rightarrow [H_2OFe^{III}XW_{11}O_{39}]^{n-} \qquad (61)$$

Electrocatalytic reduction of nitrite was carried out with the four complexes. They were each dissolved (0.45 mM) in a pH 4 buffer solution and nitrite added ($[NO_2^-]/[Fe] = \sim 40$) and the solution electrolyzed at −0.9 V. Ammonia was found as the product, with only traces of NH_2OH, and no deterioration of the catalyst was observed. An experiment was carried out in approximately the same manner with NH_2OH replacing nitrite. No ammonia was formed, indicating that the reduction process did not proceed by a sequential process through NH_2OH. It was found that the first reduction potentials of the tungsten–oxo framework and the potential where the $Fe^{III}XW_{11}O_{39}{}^{n-}$ complexes begin to catalyze the reduction of NO correlate well. This provided evidence that the electrons accepted by the NO group bound to the iron(II) come from the tungsten–oxo framework and not from the electrode. In other words, the framework serves as a reservoir of electrons which allows the NO group to be reduced in a concerted, intramolecular, multiple-electron process.

F. NITROSYL COMPLEXES

In every section of this review except Sect. I, which deals with reduced nitrogen species, Fe–NO complexes are either used as reactants or formed as products. As mentioned in the introduction, there have been about six reviews over the past dozen or so years treating nitrosyl metal complexes, and thus there is no need to repeat this material. In this section, only the more pertinent and recent findings dealing with iron–nitrosyl complexes will be described.

(i) $Fe^{2+}(aq)$

In acid solution, most iron(II) species with available coordination sites react rapidly with NO to form the $Fe^{II}(NO)$ complex. The electronic spectra due to the NO ligand usually show band maxima between 320 and 360 nm, between 420 and 460 nm, and between 580 and 660 nm [99]. For example, $FeNO^{2+}(aq)$ has bands at 340, 450, and 580 nm. Below pH 3, $FeNO^{2+}$ has a high degree of stability; however, as the pH is increased NO reduction begins to occur, and this has been studied at pH 6 (Sect. D(i)) [73,74]. The formation constant (K_1) of $FeNO^{2+}$:

$$Fe^{2+} + NO(g) \rightleftharpoons FeNO^{2+} \tag{7}$$

is 0.634 ± 0.23 atm^{-1} at 25°C over the pH range 0.5–3.3 at an ionic strength of 2.20 M. The rate constants of the formation and dissociation reactions have been measured as $k_7 = 7.1 \times 10^5$ M^{-1} s^{-1} and $k_{-7} = 1.5 \times 10^3$ s^{-1} at pH 0.6 and 25°C [99].

In order to account for the large increase in NO solubility when acetate was present in solutions with pH > 4, a dinitrosyl complex, $Fe(NO)_2^{2+}$, was proposed to form [74]. At pH 4.6 and 25°C with an acetate concentration of 2.0 M and an ionic strength of 2.20 M, the formation constant of $Fe(NO)_2^{2+}$:

$$FeNO^{2+} + NO \rightleftharpoons Fe(NO)_2^{2+} \tag{62}$$

is 0.98 ± 0.15 atm^{-1}. The structure of the dinitrosyl complex is probably octahedral with one acetate ion, two nitrosyl groups in the *cis* position and three water molecules bound to the iron. The acetate appears to enhance NO binding to the iron. The reactivity of the $Fe(NO)_2^{2+}$ complex to form N_2O indicates that the NO molecules are *cis* to one another.

There are a number of examples of dinitrosyl iron complexes which produce N_2O. One example of several reported by Hieber and Kramolowsky [100] is:

$$4[Fe(NO)_2(py)I] + 8py \rightarrow 2[Fepy_6]^{2+} + 2I^- + Fe_2O_3 + 3N_2O + 2NO \tag{63}$$

The gaseous products were determined by GC analysis.

It is of interest to note that Bhattacharyya et al. [101] have used aqueous, aerobic conditions to generate a formal iron(I) dinitrosyl species, $Fe(NO)_2^+$. In preparing the diamagnetic complex, $[Fe(NO)_2bm]_2$, where bm is benzylmercaptan or

2-mercaptoethanol, bm was added to a pH 6 solution of $FeSO_4$ and $NaNO_2$. Prior to this study, such species were produced only in organic reaction media using $[Fe(NO)_2Br]_2$ as the starting material [102].

(ii) $Fe^{II}(edta)$

When NO is bubbled into an $Fe^{II}(edta)$ solution, the color changes from light yellow to dark green with the formation of $Fe^{II}(edta)NO$,

$$Fe^{II}(edta) + NO(g) \rightleftharpoons Fe^{II}(edta)NO \tag{64}$$

having electronic spectral bands at 340, 460, and 650 nm [99]. The formation and dissociation rate constants in a pH 5.1 solution at 25°C are: $k_{64} > 6.0 \times 10^7\ M^{-1}\ s^{-1}$ and $k_{-64} > 60\ s^{-1}$. Mori et al. [103] found an equilibrium formation constant for reaction (64) of $3.48 \times 10^6\ M^{-1}$ at 38.5°C. The electrochemical oxidation of the $Fe^{II}(edta)NO$ complex results in the formation of the $Fe^{III}(edta)$ complex and nitrate [104]. When citric acid–phosphate buffer solutions were used to control the pH of reactions of $Fe^{II}(edta)$ with nitrite, the $Fe^{II}(edta)(NO)_2$ was proposed to be present in order to explain the electrochemical and spectral data [105].

The NO absorptive properties of several iron(II) complex solutions have been measured and the solution with the edta complex appears to be best in absorbing NO. The NO absorbing ability decreases with a decrease in the stability constant of the starting complex. For example, $Fe^{II}(edta)$ has a high NO absorbing ability and has a stability constant of 2.1×10^{14}, while a $Fe^{II}(glycine)$ solution, with a stability constant of 2.0×10^4, has poor NO absorbing ability [106].

(iii) Iron porphyrins

Nitric oxide adducts of iron porphyrins may be prepared in the following ways:

$$[PorFeCl] + 2NO + CH_3OH \rightarrow [PorFeNO] + CH_3ONO + HCl \quad \text{(in toluene)} \tag{65}$$

$$[PorFeCl] + 2HNO_2 \rightarrow [PorFeNO] + HNO_3 + HCl \quad \text{(in THF)} \tag{66}$$

$$[PorFe] + NO \rightleftharpoons [PorFeNO] \tag{67}$$

$$[PorFeNO] + NO \rightleftharpoons [PorFe(NO)_2] \tag{68}$$

$$[PorFeCl] + NO \rightleftharpoons [PorFeCl(NO)] \tag{69}$$

$$[PorFeClO_4] + 2NO \rightarrow [PorFe(NO)_2]^+ClO_4^- + e^- \quad \text{(electrolysis in } CH_2Cl_2\text{/hexane solution)} \tag{70}$$

Reaction (65), reductive nitrosylation, is a relatively easy way to prepare the paramagnetic [PorFeNO] which has a bent FeNO group [107,108]. Reaction (66), involving nitrous acid, may lead to some reaction with the porphyrin ring, especially if there is no substituent in the *meso* position [75]. The next three reactions ((67)–(69)) are equilibria-established with NO gas [107]. The last, reaction (70), is carried out by electrolysis of the complex in CH_2Cl_2 under an atmosphere of NO [109].

Considerable effort has been put forth to determine the nature of the six-coordinate [PorFeNO(base)] complexes [110–112]. Also, the interactions of [PorFeNO] in solution with a variety of bases have been studied in great detail, primarily using ESR spectroscopy [8–12,113,114].

Electrochemical studies of [PorFeNO] in solution have also been carried out in detail [115] and the reduction results are discussed in Sect. E(i). The electrooxidation of [TmPPFeNO], [TPPFeNO], and [OEPFeNO] in CH_2Cl_2 solution, using spectroelectrochemical techniques, has shown that, after the first oxidation, the NO remains coordinated, while with the second, the NO dissociates [116]. The values of the half-wave potentials are influenced by the porphyrin, the nature of any coordinating anion present and the solvent used. Under similar conditions, the order for the first oxidation half-wave potentials is: [TPPFeNO] > [TmPPFeNO] > [OEPFeNO]. The potential values are linearly related to the inverse of NO vibration frequencies of the [PorFeNO] complexes. Fujita and Fajer [117] considered the electrochemical nature of the porphyrin, [OEPFeNO], chlorin, [OECFeNO], and isobacteriochlorin, [(OEiBC)FeNO], and found that progressive saturation of the macrocycle made it easier to oxidize the complex. Electron abstraction appears to come from the porphyrin ring.

(iv) $[Fe_4S_3(NO)_3]^-$

A recent review of the nitrosyl complexes of Fe–S clusters [118] notes that one of the preparations of the salts containing the anion $[Fe_4S_3(NO)_3]^-$, or Roussin's black salts, is the reaction of $FeSO_4$ with $NaNO_2$ and $(NH_4)_2S$. It has recently been reported that the Na salt can be prepared by placing an aqueous solution of $FeSO_4 \cdot 7H_2O$, $NaNO_2$, and cysteine in an autoclave and heating the mixture at 118°C for 20 min [16]. Other sulfur-containing compounds, such as penicillamine and sodium thioglycolate, produce the salt in a similar manner.

G. THE TRIOXODINITRATO(−2) ANION AND OTHER N_2O_3 INTERACTIONS

There are a number of nitrite and NO reactions with iron compounds which produce N_2O. The proposed mechanisms of the reactions often include the trioxodinitrato(−2) anion, $N_2O_3^{2-}$, as a reaction intermediate. Primarily because of this, some studies on the direct reactions of the anion with certain iron compounds have been carried out. Also, dinitrogen trioxide, N_2O_3, has been proposed as an intermediate in reactions of iron compounds and a few reactions with it have been carried out. Both of these dinitrogentrioxo species will be discussed in this section.

The sodium salt, $Na_2N_2O_3$, Angeli's salt, is prepared by the reaction of butyl nitrate with hydroxylamine in a MeOH/NaOMe medium. The chemistry of this anion has been well-described [119,120]. At pH 7, $HN_2O_3^-$ forms in aqueous solution, producing N_2O and nitrite:

$$H^+ + N_2O_3^{2-} \rightarrow HN_2O_3^- \tag{71}$$

$$2HN_2O_3^- \rightarrow N_2O + H_2O + 2NO_2^- \tag{72}$$

This results from the cleavage of the N–N bond through the tautomeric form and formation of nitrosyl hydride(nitroxyl, HNO):

$$[\mathrm{O{-}\underset{1}{N}{=}\underset{2}{N}O(OH)}]^- \leftrightarrow [\mathrm{(H)O\underset{1}{N}{-}\underset{2}{N}O_2}]^- \tag{73}$$

$$HN_2O_3^- \rightarrow HNO + NO_2^- \tag{74}$$

$$2HNO \rightarrow [H_2N_2O_2] \rightarrow N_2O + H_2O \tag{75}$$

A useful technique for studying $N_2O_3^{2-}$ reactivity has been to label one of the nitrogen atoms, 1 or 2, with a ^{15}N label so that the fate of the fragment during the reaction may be determined. This labeling is possible because of the very slow rate of scrambling of the two nitrogen atoms.

(i) Fe^{2+}(aq)

The compounds, $[Co(NH_3)_6]_4[Fe^{II}(N_2O_3)_3]_3 \cdot 3H_2O$ and $[Co(NH_3)_6][Fe^{III}(N_2O_3)_3] \cdot 3H_2O$, have been prepared by reacting $FeCl_2$(aq) with a large excess of $Na_2N_2O_3$(aq) in the absence and in the presence of O_2 and with $[Co(NH_3)_6]Cl_3$ present [121]. The crystalline solids formed are sensitive to heat (50°C) and light. IR spectra indicate that the ion is bound to the iron in a bidentate mode.

Reactions of $N_2O_3^{2-}$ with Fe^{2+}(aq) have been carried out as part of a study examining the sequential reduction of NO_2^- with Fe^{2+} [73]. At pH 5–6, the reaction produces N_2O, NO and $[Fe(N_2O_3)_3]^{3-}$ by the following steps:

$$Fe(HN_2O_3)^+ \rightarrow Fe^{2+} + HNO + NO_2^- \tag{76}$$

$$NO_2^- + Fe^{2+} + 2H^+ \rightarrow Fe^{3+} + NO + H_2O \tag{77}$$

$$NO + Fe^{2+} + H^+ \rightarrow Fe^{3+} + HNO \tag{78}$$

$$2HNO \rightarrow N_2O + H_2O \tag{79}$$

The Fe^{3+} that results binds with excess $N_2O_3^{2-}$ to yield $[Fe(N_2O_3)_3]^{3-}$.

(ii) $[Fe(CN)_5NO]^{2-}$

The reaction of $N_2O_3^{2-}(aq)$ and $[Fe(CN)_5NO]^{2-}(aq)$ at pH 5–11 proceeds primarily through the following reactions:

$$[Fe(CN)_5NO]^{2-} + N_2O_3^{2-} \rightarrow [Fe(CN)_5NO]^{3-} + NO_2^- + NO \qquad (80)$$

$$[Fe(CN)_5NO]^{3-} + H_2O \rightarrow [Fe(CN)_5H_2O]^{2-} + NO^- \qquad (81)$$

$$NO^- + \tfrac{1}{2}H_2O \rightarrow \tfrac{1}{2}N_2O + OH^- \qquad (82)$$

Reaction (80) presumably proceeds in two stages. The first has $[Fe(CN)_5\text{–}(NO^+\text{–}NO^-)]^{3-}$ form through the cleavage of the N=N bond of $N_2O_3^{2-}$, production of "free" nitrite and the binding of the NO^- portion of $N_2O_3^{2-}$ to the Fe–NO group [122]. The second stage results in the loss of NO and the formation of $[Fe(CN)_5NO]^{3-}$, a complex having iron(II) and a 2e donor NO group. The next reaction (81) produces the iron(III) aquo complex, $[Fe(CN)_5H_2O]^{2-}$, and NO^-, which leads to N_2O by reaction (82). It is interesting to note that $[Ru^{II}(NH_3)_5(NO^+)]^{3+}$ reacts with $N_2O_3^{2-}$ at pH 6–14 by a very different pathway involving the immediate ion-pair formation between the reactants. This is followed by attack of the nitrosyl group on the $N_2O_3^{2-}$ [123]. It is proposed that the NO_2^- portion of $N_2O_3^{2-}$ then becomes initially bound to the metal center through the displacement of an NH_3 group, giving $[Ru^{II}(NH_3)_4(NO')(NO_2^-)]^+$, and the immediate release of NO. This eventually leads to N_2O and an unknown ruthenium product.

(iii) Iron heme centers

Metmyoglobin(Mb^+) and methemoglobin(Hb^+) react with $HN_2O_3^-$ at 25°C under anaerobic conditions to give the nitrosyl products MbNO and HbNO [124]. These reactions are alike and show that the two oxidized proteins are efficient traps for the nitroxyl species. The reaction is complex since the protein reaction is competing with the reaction forming N_2O, i.e.:

$$HN_2O_3^- \rightarrow HNO + NO_2^- \quad \text{slow} \qquad (83)$$

$$Mb^+ + HNO \rightarrow MbNO + H^+ \quad \text{fast} \qquad (84)$$

$$2HNO \rightarrow N_2O + H_2O \quad \text{fast} \qquad (85)$$

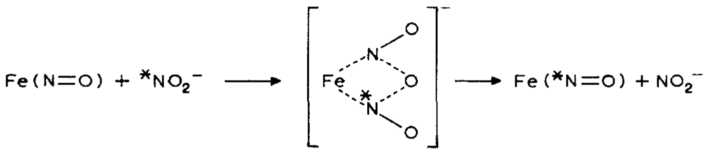
The reaction of $HN_2O_3^-$ with the reduced Hb and Mb [125] appears to involve an unknown reactive form of $HN_2O_3^-$ which goes by one or the other pathway:

$$\begin{array}{l} HN_2O_3^- \rightarrow \text{reactive form} + Hb \rightarrow Hb^+ + HbNO \quad \text{major} \qquad (86) \\ \quad\downarrow \\ \tfrac{1}{2}N_2O + NO_2^- \quad \text{minor} \end{array}$$

The nature of the reactive form is unknown. HbO_2 and MbO_2 also react with $HN_2O_3^-$ in a complex manner [126]. The participation of the apoprotein in some of these reactions has not been ruled out.

(iv) Dinitrogen trioxide reactions

The N_2O_3 group may serve as an intermediate in the exchange of nitrite and nitrosyl within the coordination sphere of iron in an intra- [127] or inter-molecular fashion. However, the N_2O_3 group is not the same species as $N_2O_3^{2-}$. Labelled nitrite, $^{15}NO_2^-$, in solution has been found to exchange rapidly with unlabeled nitrosyl found in such complexes as $[ONFe(dmdtc)_2]$ [89], $[Fe(SPr\text{-}i)_2(NO)_2]^-$ [89], and $[Fe(CN)_5NO]^{2-}$ [90]. The exchange process takes place through an initial nucleophilic attack of the $^{15}NO_2^-$ on the bound nitrosyl to form the 'W-intermediate':



(87)

Incremental amounts of N_2O_3 were added to solutions of $[Fe(TPP)]_2O$ in toluene at −95°C and the solutions warmed to room temperature in order to measure the visible spectra [128]. From these studies, reaction (88) was proposed:

$$[Fe(TPP)]_2O + 3N_2O_3 \rightarrow 2[Fe(TPP)NO_3] + 4NO \tag{88}$$

There was no evidence that an iron(III) nitrite formed using the nitrogen(III) oxide.

When the reaction of $[Fe(salen)]_2O$ with N_2O_3 at −50°C in CH_2Cl_2 was carried out, a black precipitate immediately formed [129]. The solid product was initially thought to be $[Fe(salen)NO_3]$, but it now appears to be an impure iron(III) nitrite with the chief impurity being the nitrate [130]. Any attempt to dissolve the sample produces more of the nitrate complex. The solid, when added to a CH_2Cl_2 solution of a secondary amine, such as pyrrolidine, rapidly generates the *N*-nitrosamine. This indicates that a nitrogen(III) component exists in the solid or that the solid has the potential to generate an NO^+ species to serve as the nitrosating agent. These experiments provided the impetus to examine the reaction of $[Fe(salen)]^+$ with nitrite discussed in Sect. D(iii).

H. REACTIONS OF NITROGEN(I) SPECIES

(i) Iron porphyrin nitrosyl reduction

The iron(II) porphyrin nitrosyl complex, [PorFeNO], undergoes electrochemical one-electron reduction to form $[PorFeNO]^-$. This process has been examined in some detail by Kadish [115] and the added electron appears to be on the NO group, not on the porphyrin or iron [109]. A bulk electrolysis of a solution of TPPFeNO in CH_2Cl_2 or pyridine at −1.2 or −0.98 V, respectively, resulted only in the starting material being present, even after the passage of $10\,e^-$ [131]. It was assumed that catalytic processes took place, producing reduced solvent and/or electrolyte.

When NO is bubbled into a [TPPFeNO] solution where the solvent is either $CHCl_3$, CH_2Cl_2 or C_6H_6, the following reaction occurs [113]:

$$[\mathrm{TPPFeNO}] + 3\mathrm{NO} \rightarrow [\mathrm{TPPFe(NO)(NO_2)}] + \mathrm{N_2O} \qquad (89)$$

The iron product was not isolated, but was identified by IR, EPR and UV–visible spectra. The N_2O was detected by GC. The reaction is presumed to go through a dinitrosyl adduct which then reacts with NO to give the final product (see Sect. F(i)). A product similar to $[\mathrm{TPPFe(NO)(NO_2)}]$ has been isolated from the reaction of $[\mathrm{Fe(TPP)}]_2\mathrm{O}$ and an excess of NO in toluene [128].

(ii) $[Fe(CN)_5NO]^{2-}$ reduction

As pointed out in Sect. G(ii), the reaction of $N_2O_3^{2-}$ and $[\mathrm{Fe(CN)_5NO}]^{2-}$ in water produces N_2O. One proposed path [122] for the reaction forms the intermediate $[\mathrm{Fe(CN)_5NO}]^{3-}$. This ion has been described as being an iron(II) complex bound to an NO radical; however, it produces upon hydrolysis an iron(III) complex, $[\mathrm{Fe(CN)_5H_2O}]^{2-}$, and NO^-. Therefore, it has the potential of having an $\mathrm{Fe^{III}}$–$\mathrm{NO^-}$ group. The formation of N_2O using an iron compound is a possible indication that a nitrogen(I) species is present in the iron coordination sphere.

Some aspects of the chemistry of the $[\mathrm{Fe(CN)_5NO}]^{3-}$ ion have been described. It is prepared from the nitroprusside ion, $[\mathrm{Fe(CN)_5NO}]^{2-}$, by three different methods: chemical reduction, electrochemical reduction, and continuous and pulse radiolysis. The reaction of $[\mathrm{Fe(CN)_5NO}]^{2-}$ with sodium metal in liquid ammonia produced an air-sensitive, gold-brown, paramagnetic (one unpaired electron) compound, $\mathrm{Na_3[Fe(CN)_5NO]}$ [132]. When placed into CH_3CN, a blue species, $[\mathrm{Fe(CN)_4NO}]^{2-}$, is formed. This ion has been isolated as $[\mathrm{NEt_4}]_2[\mathrm{Fe(CN)_4NO}]$ and the structure determined to be square pyramidal with an axially bound, linear NO group [133].

The $[\mathrm{Fe(CN)_5NO}]^{2-}$ ion is irreversibly reduced electrochemically at −0.82 V in either CH_3CN or CH_2Cl_2 to produce $[\mathrm{Fe(CN)_5NO}]^{3-}$, which rapidly forms $[\mathrm{Fe(CN)_4NO}]^{2-}$ [134]. This ion is oxidized and reduced reversibly:

$$[\mathrm{Fe(CN)_4NO}]^{-} \xrightleftharpoons[-e^-,\,-0.66\,\mathrm{V}]{} [\mathrm{Fe(CN)_4NO}]^{2-} \xrightleftharpoons[+e^-,\,-1.23\,\mathrm{V}]{} [\mathrm{Fe(CN)_4NO}]^{3-} \qquad (90)$$

If $[\mathrm{Fe(CN)_4NO}]^{2-}$ undergoes bulk electrolysis near −1.23 V, a green product forms which converts in air to a diamagnetic yellow-orange product. The nature of these products is unknown.

When an aqueous solution of $[Fe(CN)_5NO]^{2-}$ is subjected to continuous and pulse radiolysis over a pH range of 1–8.5, $[Fe(CN)_5NO]^{3-}$ forms with a visible spectrum independent of pH [135]. The rate of formation of $[Fe(CN)_5NO]^{3-}$ has been determined using the following species (rate constant, $M^{-1} s^{-1}$): $e^{-}aq$ (1.0×10^{10}); CO_2^{-} (4.0×10^{8}); $\cdot CH_2OH$ (6.7×10^{8}); $(CH_3)_2COH$ (2.9×10^{9}) and H (7×10^{7}). The product rapidly establishes the equilibrium:

$$Fe(CN)_5NO]^{3-} \rightleftharpoons [Fe(CN)_4NO]^{2-} + CN^{-} \tag{91}$$

with a rate of formation of $2.8 \times 10^{2}\ s^{-1}$ and an equilibrium constant of 6.8×10^{-5}. Both values are independent of pH (4.6–8.5) and the radical species used to form $[Fe(CN)_5NO]^{3-}$. The equilibrium shifts to the right with a decrease in pH. If the solution is exposed to O_2, polymeric species, $[Fe(CN)_5NO]^{2-}$, and $[Fe(CN)_4NO(OH)]^{2-}$ form. If $CH_2C(CH_3)_2OH$ is used as a reactant, the air-insensitive ion, $[Fe(CN)_5N(O)CH_2C(CH_3)_2OH]^{3-}$ forms with a rate constant of $2.5 \times 10^{9}\ M^{-1} s^{-1}$.

No mention of N_2O formation was made in either the electrochemical reduction or radiolysis reports. There does not appear to have been any detailed study made of the hydrolysis of $[Fe(CN)_5NO]^{3-}$ to form N_2O.

Two reactions which produce N_2O but probably do not involve an $Fe{-}NO^{-}$ group are the reactions of $[Fe(CN)_5NO]^{2-}$ with N_3^{-} and NH_2OH [136]. The first

$$[Fe(CN)_5NO]^{2-} + N_3^{-} + H_2O \rightarrow [Fe(CN)_5H_2O]^{3-} + N_2 + N_2O \tag{92}$$

proceeds rapidly ($\text{Rate} = {\sim}0.2\ M^{-1} s^{-1}[[Fe(CN)_5NO]^{2-}][N_3^{-}]$). The second reaction

$$[Fe(CN)_5NO]^{2-} + NH_2OH \rightarrow [Fe(CN)_5H_2O]^{3-} + N_2O + H_2O \tag{93}$$

is very fast. The pathways of these reactions involve nucleophilic attack of the N_3^{-} and NH_2OH on the coordinated nitrosyl, possibly forming intermediates with unusual structures.

I. REACTIONS WITH REDUCED NITROGEN SPECIES

(i) Hydroxylamine

The oxidation of NH_2OH by $[Fe(CN_6)]^{3-}$ [137] and $Fe^{3+}(aq)$ [138] has been found to be catalyzed by Cu^{2+} to produce N_2 and N_2O, respectively.

$$2NH_2OH + 2[Fe(CN)_6]^{3-} \rightarrow N_2 + 2[Fe(CN)_6]^{4-} + 2H_3O^{+} \tag{94}$$

$$2NH_3OH^{+} + 4Fe^{3+} \rightarrow 4Fe^{2+} + N_2O + 6H^{+} + H_2O \tag{95}$$

Reaction (94) is also catalyzed by Fe^{III}(edta), and reaction (95) is carried out in strongly acid solutions. Both reactions have been examined because of their potential to serve as methods for the quantitative analysis of NH_2OH. The rate laws are complex; however, the first step proposed in both mechanisms is the binding of the catalyst with NH_2OH. This intermediate goes on to react with the iron(III) species and, ultimately, give the products. Hieber and Beutner [139] found that NH_2OH reacts with $[Fe(CO)_4]^{2-}$ to yield $[Fe(CO)_3NO]^-$ and $[Fe(CO)_3NH]_2$.

(ii) Nitroso compounds

The iron(III) porphyrin [TPPFeCl] reacts with 2-hydroxyaminopropane in a 1:2 ratio in chloroform at 20°C under argon to produce the nitroso complex, [TPPFe(i-PrNO)(i-PrNH(OH))] [140,141]. The hydroxylamine can be readily displaced by a base (L). The nitroso complex can also be obtained from the iron(II) complex:

$$\begin{tikzcd}
\text{[TPPFeCl]} + \text{i-PrNHOH} \arrow[r, "CHCl_3", "\text{Ar}, 20^{\circ}\text{C}"'] & \text{[TPPFe(i-PrNO)(i-PrNHOH)]} \arrow[d, "+\text{L}", "-(\text{i-PrNHOH})"'] \\
& \text{[TPPFe(i-PrNO)(L)]} \\
& \text{[TPPFe]} + \text{i-PrNO}(\rightleftharpoons 0.5(\text{i-PrNO})_2) \rightarrow \text{[TPPFe(i-PrNO)]} \arrow[u, "+\text{L}"']
\end{tikzcd} \tag{96}$$

where L = py, $i\text{-}PrNH_2$, N-Meim, MeOH, or $PPhMe_2$.

The overall reaction in py is:

$$2[PorFeCl] + 3RNHOH \rightarrow 2[PorFe(RNO)(py)] + RNH_2 + H_2O + 2HCl \tag{97}$$

The nitroso complexes are stable indefinitely away from air, but slowly decompose in air to produce the μ-oxo complex. The RNO ligand is not displaced from the complex by CO and is considered to be a strong π-acid. The structure of [TPPFe(i-PrNO)(i-$PrNH_2$)] shows the nitroso ligand to be attached to the Fe atom through the N atom with a relatively short bond (1.86 Å) and to have a CNO angle of 116° [140] (Fig. 4). Watkins and Balch [142] examined the NMR spectra of [PcFe] in $CDCl_3$ with some aromatic nitroso compounds and n-$BuNH_2$ present. In order to explain the NMR spectra of the [PcFe(RNO)(n-$BuNH_2$)] complexes, it was necessary that the nitroso compound bind to the Fe atom through the N atom. The 'end-on' bonding mode of RNO to Fe, rather than a 'side-on' mode, make the interaction of RNO similar to that of O_2 bonding. The resonance Raman and Mössbauer spectra of the nitroso compounds are very similar to those of the O_2 complexes.

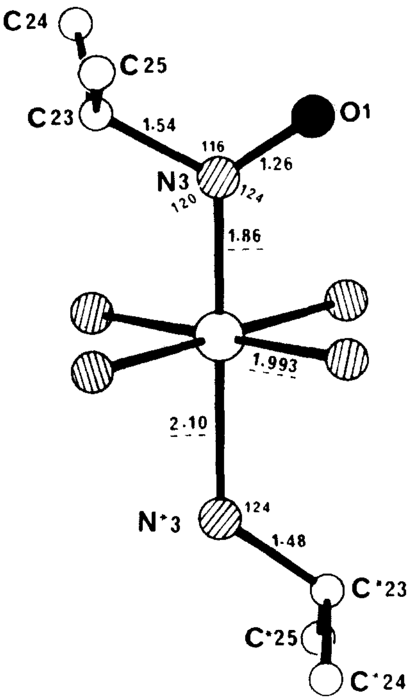
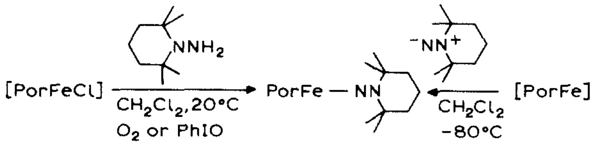


Fig. 4. Representation of the ligand positions in [TPPFe(i-PrNO)(i-PrNH$_2$)] (only the nitrogen atoms of the porphyrin are represented). (Reproduced with permission from ref. 140.)

(iii) Nitrenes

The two compounds 1-amino-2,2,6,6-tetramethylpiperidine and [(tosylimino)-iodo]benzene produce two unusual compounds when reacted with [PorFeCl]. The product from the piperidine or hydrazine derivative can be obtained in three ways [143,144].



(98)

The air-stable compound formed has a linear Fe–N–N group with bond distances for Fe–N of 1.81 Å and for N–N of 1.23 Å (Fig. 5). The product is a high-spin iron(II) complex similar to [PorFe^{II}(imidazole)].

The product of the reaction of PhI=NTs and [PorFeCl] using several different porphyrins in CH$_2$Cl$_2$ at 20°C is [PorFe(NTs)Cl], which has a tosyl nitrene group being inserted between the iron and one of the porphyrin nitrogens [145]. This

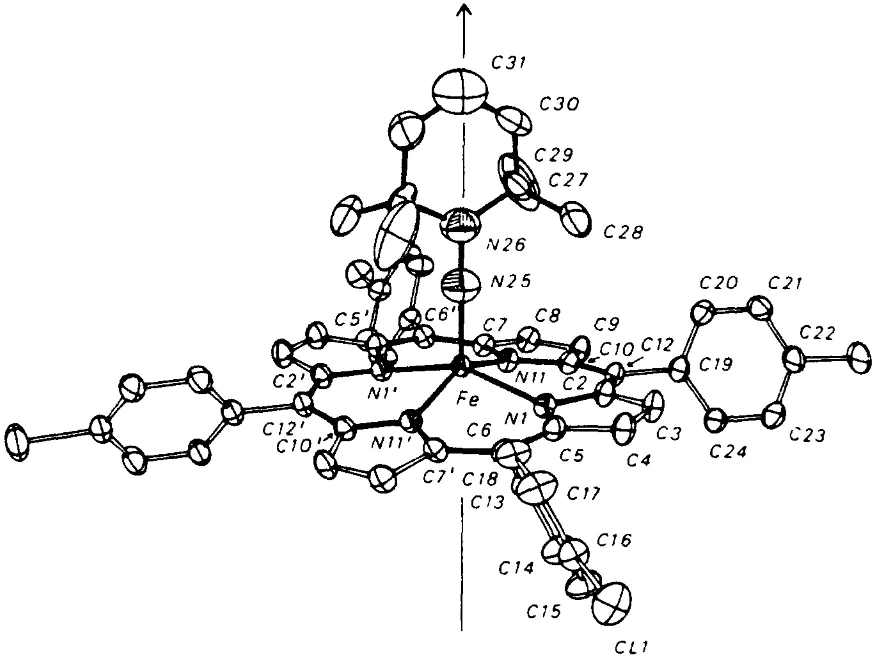
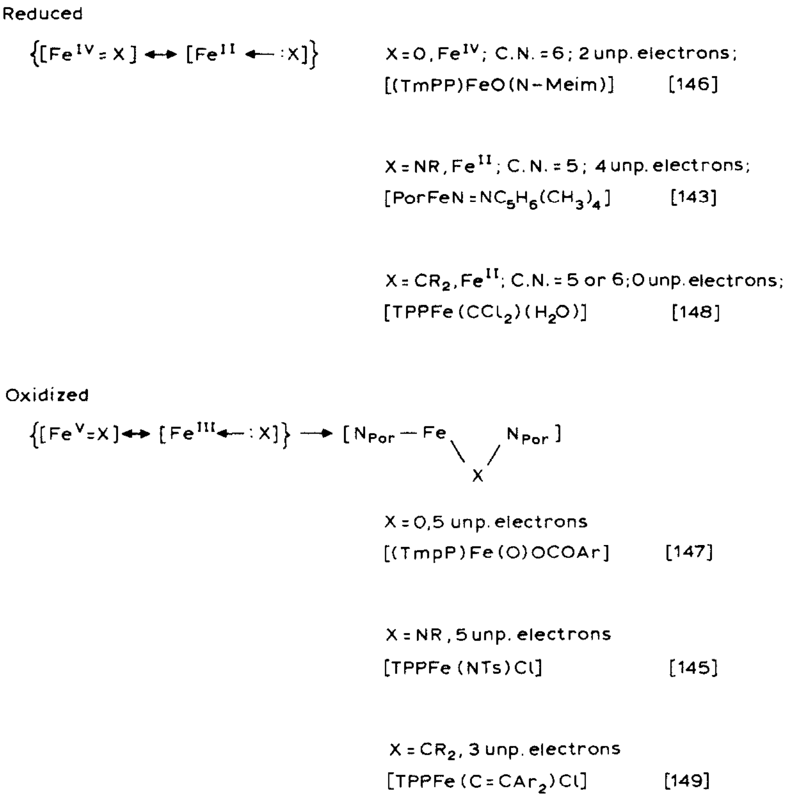


Fig. 5. Structure of [TpClPPFe(NNC_9H_{18})]. (Reproduced with permission from ref. 143.)

severely distorts the porphyrin ring and makes iron have a distorted trigonal bipyramid ligand arrangement. The structure of [TPPFe(NTs)Cl] shows that the nitrene N, Cl, and one porphyrin N are in the equatorial plane with the remaining two porphyrin Ns serving as the axial ligands. The products appear to be high-spin iron(III) complexes.

The relationship between the two nitrene products and similar oxygen and carbon compounds is shown in Scheme 2 ($X=O$, NR, or CR_2). The [PorFeN=$NC_5H_6(CH_3)_4$] product is pentacoordinate and high spin ($S=2$). It has an electron distribution best represented by $Fe^{II}\leftarrow :NR$, rather than $Fe^{IV}=NR$. The oxygen compound is more like $Fe^{IV}=O$, possibly because of the high electronegativity of oxygen. Removing an electron would lead to an iron(V) or iron(III) oxidized form; however, it appears to rearrange to the insertion product where the X group inserts between the Fe atom and one porphyrin N. The N example is the product of the reaction between the N-analog of iodosyl benzene and the iron(III) porphyrin chloride. It is a high-spin ($S=\frac{5}{2}$) iron(III) complex. The intermediate spin ($S=\frac{3}{2}$) state of the carbon insertion complex may result from the high strength of the Fe–C bond. The oxygen insertion complex, [(TmPP)Fe(O)OCOAr], may oxidize nitrite to nitrate using the inserted oxygen atom. Such a reaction would mimic that of catalase I [149].



Scheme 2.

(iv) Nitride

The nitrido complexes, [$(TPPFe)_2N$] and [$(PcFe)_2N$], have been prepared through the thermal decomposition of the azide ion. Heating [$TPPFeN_3$] in refluxing xylene for 14 h produces [$(TPPFe)_2N$] [150], while when a mixture of [PcFe] is heated with NaN_3 in α-chloronaphthalene [$(PcFe)_2N$] results [151]. The oxidation of [$(PcFe)_2N$] with Cp_2Fe^+ has led to the isolation of $[(PcFe)_2N]^+[PF_6]^-$ [151] and $[(LPcFe)_2N]^+[PF_6]^-$ where L is py, pip, 1-Meim or 4-Mepy [152]. The structure of [$(TPPFe)_2N$] shows a linear Fe–N–Fe group with a porphyrin skeleton which deviates from planarity [153].

The electrochemistry of [$(TPPFe)_2N$] and [$(PcFe)_2N$] in py have been compared [151]. The potentials (vs. SCE) for the one-electron oxidation and reduction processes for the two macrocyclic complexes are as follows:

$$\underset{\substack{\text{Pc}\\ \text{TPP}}}{[(\text{PorFe})_2\text{N}]^+} \underset{\substack{0.00\\ -0.25}}{\overset{-e}{\rightleftharpoons}} [(\text{PorFe})_2\text{N}] \underset{\substack{-0.83\\ -1.04}}{\overset{+e}{\rightleftharpoons}} [(\text{PorFe})_2\text{N}]^-$$

$$\underset{\substack{-1.02\\ -1.52}}{\overset{+e}{\rightleftharpoons}} [(\text{PorFe})_2\text{N}]^{2-} \underset{\substack{-1.29\text{V}\\ -1.69}}{\overset{+e}{\rightleftharpoons}} [(\text{PorFe})_2\text{N}]^{3-} \qquad (99)$$

The more negative values for the TPPFe complexes are due to the more basic nature of the TPP macrocycle compared with that of Pc. The 1 e^- oxidation of $[(TPPFe)_2N]$ has been considered in some detail by Kadish et al. [154].

The formation of $[(PorFe)_2N]^+$ and $[(PorFe)_2N]^-$ is reversible, showing Nernstian behavior, while the $[(PorFe)_2N]^{2-}$ and $[(PorFe)_2N]^{3-}$ formation result in some decomposition to [TPPFe]. Controlled potential electrolysis of a py solution of $[(TPPFe)_2N]$ at -1.65 V results in the spectrum of $[TPPFe(py)_x]^-$ after 5 equivalents of charge per dimer. The fate of the nitrogen bridge was not determined, but it is assumed to have formed NH_3 or NH_2^- with trace water.

A large number of iron clusters containing nitrosyl and nitrido ligands have been described in a recent review [28]. The majority of the nitrido clusters are tetrairon clusters with one nitrido ligand and a number of carbonyl groups. One example is $\{Fe_4N(CO)_{12}]^-$, which is formed by the reaction of $[Fe(CO)_3(NO)]^-$ and $[Fe_3(CO)_{12}]$. The structure shows four iron atoms arranged in a square with the nitrogen atom 0.093 Å below the square plane of iron atoms.

(v) Azide

Except for the formation of the μ-nitrogen complexes under rather severe conditions, azide iron complexes are stable toward reactivity. There are many azide–iron(III) complexes, especially iron(III) porphyrins. N_3^- has been used as a counterion in the electrochemistry of $[PorFe^{III}]^+$ in non-aqueous media [115]. The electrochemical nature of iron(III) quadridentate Schiff base azide complexes has also been examined [155]. No unusual effects have been reported in the electrochemistry of these complexes.

(vi) Ammonia

The iron(III) porphyrin diammine complex, $[TPPFe(NH_3)_2]^+$, has recently been reported [156], while the Fe(II) complex, $[OEPFe(NH_3)_2]$, is made in an unusual reaction [157]:

$$[\text{TPPFe}(\text{SO}_3\text{CF}_3)] + 2\text{NH}_3(\text{g}) \xrightarrow{\text{CH}_2\text{Cl}_2} [\text{TPPFe}(\text{NH}_3)_2]^+ + \text{SO}_3\text{CF}_3^- \qquad (100)$$

$$[\mathrm{OEPFeCl}]+\mathrm{N_2H_4\cdot H_2O}\xrightarrow{\text{2-Mepy}}[\mathrm{OEPFe(NH_3)_2}] \tag{101}$$

If reaction (101) is carried out using py, 3-Mepy or 4-Mepy as a solvent instead of 2-Mepy, the reduced adduct, [OEPFeL$_2$], is formed. The +3 complex has been formed in solution and is low-spin. The +2 complex has been isolated in the solid state and is low-spin.

(vii) Amines

A large number of iron(II) and iron(III) porphyrin amine adducts have been described [158]; however, certain primary and secondary amines have been found to react with [PorFeCl]. The first report described the rapid formation of an iron(II) adduct, [TPPFe(pip)$_2$], when [TPPFeCl] was mixed with piperidine [159].

Castro et al. [160] have examined the reaction of [PorFeCl] with the amines in some detail. In order to react the amine must coordinate to iron and possess the

$\rangle\mathrm{CH\underset{H}{N}R}$ moiety. The overall reaction in C_6H_6 and DMF is:

$$2[\mathrm{PorFe^{III}Cl}]+7\mathrm{RNH_2}\rightarrow2[\mathrm{PorFe^{II}(H_2NR)_2}]+\mathrm{R'CH{=}NH}+2\mathrm{RNH_3^+Cl^-} \tag{102}$$

with the only redox product of the amine being the imine. The reaction goes through four steps:

1. Ligation

$$2\mathrm{RNH_2}+[\mathrm{PorFe^{III}Cl}]\rightarrow[\mathrm{PorFe^{III}(RNH_2)_2}]^+ +\mathrm{Cl^-} \tag{103}$$

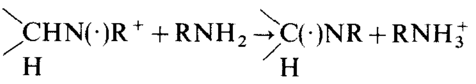
where the addition of one amine is fast, while the second one adds slowly.

2. Outer-sphere reduction

$$[\mathrm{PorFe^{III}(RNH_2)_2}]^+ +\mathrm{RNH_2}\rightarrow[\mathrm{PorFe^{II}(RNH_2)_2}]+\mathrm{RN(\cdot)H_2^+} \tag{104}$$

with the formation of the aminium cation radical.

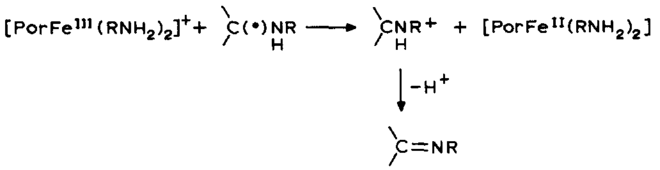
3. The formation of α-aminocarbinyl radical



$$\rangle\mathrm{CH\underset{H}{N}(\cdot)R^+}+\mathrm{RNH_2}\rightarrow\rangle\mathrm{C(\cdot)\underset{H}{N}R}+\mathrm{RNH_3^+} \tag{105}$$

by either a direct or indirect reaction.

4. A second outer-sphere redox reaction



(106)

A way to examine amine–iron(III) porphyrin interactions in solution is to add an equivalent of CN^- to the $[PorFe^{III}]^+$ DMSO solution, then four equivalents of amine [161]. The low-spin [PorFeCN(amine)] is formed and its NMR spectrum measured.

J. A FINAL COMMENT

One recent development reported by Suslick and Watson [162] is the photochemical activation of the porphyrin complex, $[Fe(TPP)NO_3]$. When an oxygen-free solution of this complex is irradiated in the 350–450 nm region in the presence of $P(C_6H_5)_3$ or styrene, all three of the nitrate oxygen atoms are transferred to the substrate. The ultimate fate of the nitrogen is unknown. The photochemical nature of many of the compounds treated in this review might be worthy of consideration.

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