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Supplementary Material Available: Anisotropic thermal parameters, hydrogen positional and thermal parameters, and observed and calculated structure factors for $ReH_4AlMe_2(PPh_2Me)_3$ and $ReH_6AlMe_2(PPh_2Me)_2$ (66 pages). Ordering information is given on any current masthead page.

Reactions of the Tris(3,4,7,8-tetramethylphenanthroline)iron(II,III) Redox Couple in Nitrous Acid

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Abstract: The kinetics and mechanisms of the redox reactions of $[Fe(TMP)_3]^{2+/3+}$ (TMP = 3,4,7,8-tetramethylphenanthroline) with nitrous acid have been investigated in aqueous solution at 25.0 °C in sulfate media. With a large excess of nitrite, $[Fe(TMP)_3]^{3+}$ at pH >2 is reduced quantitatively to $[Fe(TMP)_3]^{2+}$ with non-pseudo-first-order kinetics; the reaction is strongly inhibited by $[Fe(TMP)_3]^{2+}$. Acid also inhibits the reaction, but there is a direct dependence on $[NO_2^-]$. The proposed mechanism involves protonation of NO_2^- to form unreactive HNO_2; NO_2^- is oxidized quasi-reversibly by $[Fe(TMP)_3]^{3+}$ to form NO_2 with a rate constant, k_1, of 3.9×10^3 M^{-1} s^{-1}, and then NO_2 disproportionates to form NO_3^- and NO_2^-. At pH ≤1 $[Fe(TMP)_3]^{2+}$ is quantitatively oxidized in nitrous acid with pseudo-first-order kinetics; the reaction is strongly inhibited by NO. In the presence of added NO the rate law shows one term first order in $[HNO_2]$ and another term approximately second order in $[HNO_2]$. The path first order in $[HNO_2]$, which is undetectably slow in the absence of added NO, has a rate constant of 95 M^{-1} s^{-1}, and it is interpreted as the direct reduction of HNO_2. The path second order in $[HNO_2]$ is inverse in [NO], and it is interpreted as the rapid equilibrium formation of NO_2 and NO by disproportionation of HNO_2, followed by rate limiting ($k_{-1} = 2.0 \times 10^6$ M^{-1} s^{-1}) reduction of NO_2 by $[Fe(TMP)_3]^{2+}$. This last step is the microscopic reverse of the rate-limiting step for the reaction of NO_2^- with $[Fe(TMP)_3]^{3+}$. The equivalence of the ratio k_1/k_{-1} and the thermochemically determined equilibrium constant confirms the mechanistic assignments. The combined effects of reversible reduction of HNO_2 to NO and irreversible oxidation of HNO_2 to NO_3^- lead to biphasic kinetics in the pH range 1-2.

The chemistry of reactions with nitrous acid is broad and complex.[1-3] Aqueous solutions of nitrous acid contain a variety of minor components, many of which can be reactive. Third-order rate laws have often been reported for reactions which are first order in substrate, acidity, and N(III); such reactions are thought to proceed by a two-step mechanism in which protonation of HNO_2 yields NO^+ and then NO^+ reacts with the substrate in the rate-limiting step.[1] In several cases these NO^+ pathways have been reported for single electron oxidations of substitution inert coordination complexes;[4,5] for reactions such as these the product should be NO. Thus the rate-limiting step may involve the NO/NO^+ couple in an outer-sphere electron-transfer reaction.

Our continuing interest in the kinetics of outer-sphere redox reactions has recently embraced the notion that nuclear tunneling may be a rather significant factor, particularly for the NO_2/NO_2^- couple.[6] This is due to the high frequency of the vibrational modes that are coupled with electron transfer. The high frequencies for NO and NO^+ suggest that nuclear tunneling could be especially prominent in NO^+ pathways. The O_2/O_2^- couple is in many ways analogous with the NO/NO^+ couple. The proposal that the O_2/O_2^- couple behaves consistently with Marcus-Hush theory[7] has recently been questioned.[8] In an attempt to investigate these ideas, a study of the reactions of $IrCl_6^{3-}$ in nitrous acid was undertaken. The reaction presented unexpected difficulties, and so we were forced to reassess the body of results published on similar systems.

Particularly intriguing was a recent report[9] on the reaction of $[Fe(TMP)_3]^{2+/3+}$ (TMP = 3,4,7,8-tetramethylphenanthroline) in nitrous acid; biphasic kinetics for the reaction of $[Fe(TMP)_3]^{2+}$ were reported, and for the first phase paths were found first order in $[NO_2^-]$ and first order in $[HNO_2]$, but no NO^+ path was found. The reactions were performed in chloride-containing media; the possibility that the unusual results were due to reactivity of NOCl encouraged us to reinvestigate the reaction in chloride-free media. In the course of these studies, the reaction was found to be unexpectedly sensitive to the presence of nitric oxide. This observation entailed an extensive reinvestigation of the system. The rate law differs substantially from the prior report, but there is still no evidence for a NO^+ pathway. It is now questionable whether such a pathway has actually been observed for any outer-sphere reactions.

Experimental Section

Materials. $Li_2SO_4 \cdot H_2O$ was prepared by neutralizing Li_2CO_3 (Baker) with an appropriate amount of concentrated H_2SO_4 (MCB). The salt was recrystallized from warm water twice such that its solutions gave neutral pH.[10] $Na_4P_2O_7 \cdot 10H_2O$ (Baker) was recrystallized from warm water.[10] This buffer was used in the pH range 4-6; orthophosphate was found to be unsuitable as a buffer due to the insolubility of its lithium salt. $LiNO_3$ was prepared by neutralizing Li_2CO_3 with concentrated HNO_3 and it was recrystallized from hot water.[10] Its solutions were

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tested to be neutral. $NaNO_2$ was recrystallized by dissolving $NaNO_2$ (Mallinckrodt) in 50% aqueous ethanol at ~80 °C and cooling the solution in the refrigerator.

$[Fe(TMP)_3]SO_4$ was prepared by mixing approximately 200 mg of TMP (3,4,7,8-tetramethylphenanthroline) (G. F. Smith) with 50 mg of $FeSO_4{\cdot}7H_2O$ in 5 mL of water–ethanol (95:5) mixture, adding 5 mL of saturated Na_2SO_4 solution, and cooling in the refrigerator for 1 h. The product was washed with ether and suction dried. The perchlorate, nitrate, and trifluoromethanesulfonate salts of $[Fe(TMP)_3]^{2+}$ were extremely insoluble; the chloride salt and chloride media were not used in order to avoid complications arising due to the formation and reactions of NOCl.[1]

Although the perchlorate salt of $[Fe(TMP)_3]^{3+}$ has been prepared,[11] it was not suitable for our kinetic studies due to the insolubility of the $[Fe(TMP)_3]^{2+}$ product. The sulfate salt of the complex $[Fe(TMP)_3]_2(SO_4)_3$ was stable only when in contact with acid; attempts to isolate the pure salt produced a material that rapidly decomposed to $[Fe(TMP)_3]^{2+}$. Difficulties in handling $[Fe(TMP)_3]^{3+}$ solutions have been reported.[12] We experienced the same difficulties. The following two procedures involved minimal $[Fe(TMP)_3]^{3+}$ decomposition, and both procedures gave $[Fe(TMP)_3]^{3+}$ solutions that gave identical kinetic results. (i) $[Fe(TMP)_3]^{3+}$ solutions at 4×10^{-3} M in 1 M H_2SO_4 were prepared in the following manner. About 30 mg of $[Fe(TMP)_3]SO_4$ was stirred in 1 M H_2SO_4. About 200 mg of black PbO_2 (MCB) was added and the stirring continued for 5 min. The excess PbO_2 and $PbSO_4$ product was filtered off twice with a medium frit. About 0.1 mL of this solution was diluted to 10 mL and used for kinetic studies. The pH of the solution was adjusted with NaOH and H_2SO_4. (ii) $[Fe(TMP)_3]SO_4$ in 0.1 M Li_2SO_4 was oxidized with a Pt wire mesh electrode at +0.95 V vs. SCE. The solution was kept stored with the positive potential applied. The pH of the solution was adjusted with H_2SO_4 solutions of appropriate concentration. These Fe(III) solutions were used within 3 h of their preparation.

Argon (Matheson) was purified by bubbling it through a chromous tower; nitric oxide (Matheson) was scrubbed free of NO_2 by passing it through aqueous sodium hydroxide or a moist Ascarite column. Solutions were first deoxygenated with argon to remove all dissolved oxygen (15 min) and then bubbled with a brisk flow of nitric oxide for 10 min.

All solutions were prepared from deionized and distilled water, were permitted to contact only glass, Teflon, and platinum, and were sparged with argon to remove oxygen.

Analyses. The purity of $NaNO_2$ was initially checked by the OCl^- oxidation methods,[13] NaOCl solutions being substituted for $Ca(OCl)_2$ solution. Since its purity was found to be 100 (±2)%, stock solutions for later experiments were prepared by dissolving accurately known weights (~1.4 g) and diluting in volumetric flasks (25 mL). This stock solution was further diluted as required, and known volumes of these diluted solutions were used for the stopped flow experiments.

The spectra of $[Fe(TMP)_3]^{2+}$ and $[Fe(TMP)_3]^{3+}$ showed λ_{max} and ϵ values as reported in literature.[11] Where necessary, the $[Fe(TMP)_3]^{2+}$ concentrations were determined from measured absorbance values at 500 nm (ϵ 1.38×10^4 M^{-1} cm^{-1}).[11]

Lithium sulfate and lithium nitrate solutions were standardized by cation exchange with H^+ form of the Dowex 50W-X8 cation exchanger and titration against standardized 0.1 M NaOH solution.

The pH of the solutions were measured directly by using a Corning 130 pH meter calibrated with standard pH solutions, and UV/vis spectra were recorded on a Cary 210 spectrophotometer with 1-cm quartz cells.

Experiments with added NO were performed by mixing equal volumes of NO-free and NO-saturated solutions. The concentration of NO was taken as half the saturation concentration (1.9×10^{-3} M[14]).

Determination of $[Fe(TMP)_3]^{2+/3+}$ Redox Potential. A potentiometric titration of 30 mL of 6.6×10^{-4} M $[Fe(TMP)_3]SO_4$ in 0.3 M H_2SO_4 against 4.8×10^{-3} M $(NH_4)_4Ce(SO_4)_4$ solution in 0.3 M H_2SO_4 was carried out by measuring the potential of a Pt electrode relative to a 3.5 M NaCl calomel electrode with the Corning 130 pH meter. The potential at half equivalence was stable at 0.569 V. The reference electrode potential (0.272 V vs. NHE in 0.3 M H_2SO_4) was obtained by calibration relative to SCE (0.245 V). This leads to a potential vs. NHE of 0.84 V for $[Fe(TMP)_3]^{2+/3+}$ in 0.3 M H_2SO_4, which is in agreement with that estimated in ref 21.

Kinetics. Kinetics data were collected at 500 nm at 25.0 °C by using the stopped-flow apparatus as described previously.[6,15]

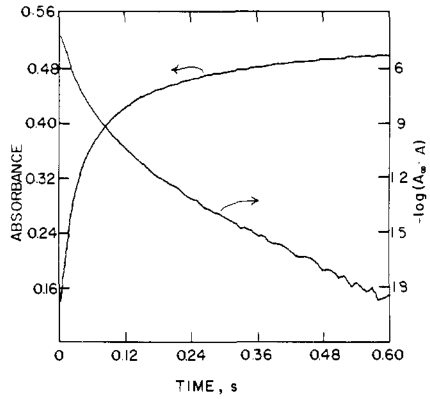

Figure 1. Non-pseudo-first-order reaction of NO_2^- with $[Fe(TMP)_3]^{3+}$ ($[NO_2^-] = 4.0 \times 10^{-3}$ M; pH 7).

The $[Fe(TMP)_3]^{3+}$ reactions with N(III) were performed at 0.3 and 3.0 M ionic strengths (Li_2SO_4). The observed pseudo-first-order rate constants were obtained from initial slopes of semilog plots of log ($A_\infty - A_t$) vs. time. Pyrophosphate buffer ($pK_2 = 4.77$[16]), 1.0×10^{-3} M, was used for pH >4, and nitrite buffer ($pK_a = 2.9$[17]), 1.0×10^{-2} M, was used for experiments at pH <4.

The reactions of HNO_2 with $[Fe(TMP)_3]^{2+}$ were carried out at μ = 1.0 M (Li_2SO_4–H_2SO_4) media. Kinetics were monitored by following the disappearance of the Fe(II) complex. The reactions, except where premixed HNO_2 was used, were initiated by mixing an acidic HSO_4^- solution with a solution of $[Fe(TMP)_3]^{2+}$ and $NaNO_2$. For the experiments with added nitric oxide, the acid solutions were saturated with nitric oxide. Pseudo-first-order rate constants were obtained by exponential fits to the observed absorbance data. When premixed HNO_2 was used, a deoxygenated solution of $NaNO_2$ was acidified and then transferred to the stopped-flow apparatus; approximately 3 min elapsed between acidification and initiation of the reaction with $[Fe(TMP)_3]^{2+}$

The $[Fe(TMP)_3]^{3+}$ reactions with NO were performed at μ = 0.3 M (Li_2SO_4) with [NO] = 9.5×10^{-4} M and $[Fe(TMP)_3]^{3+} \approx 2.0 \times 10^{-5}$ M at 25.0 °C in the pH range 1.2–7.0. Phthalate buffer ($pK_a = 4.0$[16]), 1.0×10^{-3} M at pH 4.0, pyrophosphate buffer for pH >4.0, and the sulfate medium ($pK_a = 1.9$[16]) for pH <4 were used to control pH. The reactions were initiated by mixing saturated nitric oxide solutions with buffered $[Fe(TMP)_3]^{3+}$ solutions in Li_2SO_4. Excellent pseudo-first-order kinetics were obtained, and the rate constants were obtained by exponential fits to the data.

Rate laws 2, 4, and 5 were fitted to the data by using the Los Alamos nonlinear least-squares program on a PDP 11/70 computer. Data were weighted as $1/k_{obsd}$. Errors indicated are one standard deviation.

Results

The behavior of the $[Fe(TMP)_3]^{2+/3+}$ redox couple in solutions of nitrous acid is fairly complex. However, there are conditions under which the various processes can be isolated. Thus at low acidity $[Fe(TMP)_3]^{3+}$ is quantitatively reduced to $[Fe(TMP)_3]^{2+}$; at high acidity $[Fe(TMP)_3]^{2+}$ is quantitatively oxidized to $[Fe(TMP)_3]^{3+}$. Furthermore, NO, which is formed at high acidity and which reacts with $[Fe(TMP)_3]^{3+}$, can be studied independently of nitrous acid simply by preparing solutions with NO as a reagent. These three series of experiments are described below.

$[Fe(TMP)_3]^{3+}$ + NO_2^-. The consumption ratio, $\Delta[Fe(TMP)_3]^{3+}/\Delta NO_2^-$, was found to be 1.9 (±10)% as judged by the yield of $[Fe(TMP)_3]^{2+}$ in an experiment with $[Fe(TMP)_3]_0^{3+} = 4.5 \times 10^{-4}$ M and $[NaNO_2] = 5.0 \times 10^{-5}$ M in 0.1 M Li_2SO_4 at pH 7.0. The product spectrum had λ_{max} and ϵ corresponding to $[Fe(TMP)_3]^{2+}$.[11] The reaction can be given as shown in eq 1.

$$H_2O + 2[Fe(TMP)_3]^{3+} + NO_2^- \rightarrow 2[Fe(TMP)_3]^{2+} + NO_3^- + 2H^+ \quad (1)$$

This result is analogous to studies using other oxidants.[18] A study

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Table I. Kinetics Results for the Reaction of $[Fe(TMP)_3]^{3+}$ with NO_2^- in the Presence of Added Reagents[a]

$[NaNO_2]$, M	k_{obsd}, s^{-1}	added reagent
1.0×10^{-2}	19.1	$\mu = 3.0$ M
4.0×10^{-3}	6.4	$\mu = 3.0$ M
1.0×10^{-3}	1.7	$\mu = 3.0$ M
1.0×10^{-2}	37.5	0.02 M $LiNO_3$
1.0×10^{-2}	19.7[b]	5×10^{-4} M TMP
1.0×10^{-3}	3.8	1.8×10^{-4} M $NiSO_4$
1.0×10^{-3}	3.7	no $P_2O_7^{4-}$
1.0×10^{-2}	38.0	1.0×10^{-3} M O_2
1.0×10^{-2}	10.5	4.5×10^{-5} M $[Fe(TMP)_3{}^{2+}]_0$
4.0×10^{-3}	4.3	4.5×10^{-5} M $[Fe(TMP)_3{}^{2+}]_0$

[a] $\mu = 0.3$ M (Li_2SO_4); pH 7.0; $[Fe(TMP)_3{}^{3+}]_0 \approx 2.0 \times 10^{-5}$ M; 25.0 °C; $[Na_4P_2O_7] = 1.0 \times 10^{-3}$ M. [b] pH 3.1.

Table II. Kinetics Results for the Reaction of $[Fe(TMP)_3]^{3+}$ with NO_2^-[a]

$[NaNO_2]$, M	pH	k_{obsd}, s^{-1}	k_{calcd},[b] s^{-1}
1.0×10^{-2}	6.8	41.5[c]	39.4
1.0×10^{-2}	5.6	41.5[c]	39.3
1.0×10^{-2}	4.2	37.0[c]	37.0
1.0×10^{-2}	3.1	21.5	21.7
1.0×10^{-2}	2.4	11.4	13.5
1.0×10^{-2}	2.0	3.8	3.5
7.0×10^{-3}	7.0	26.8[c]	26.8
4.0×10^{-3}	7.0	16.7[c]	15.8
2.0×10^{-3}	7.0	7.4[c]	7.9
1.0×10^{-3}	7.0	3.8[c]	3.9
4.0×10^{-4}	7.0	1.61[c]	1.58

[a] $\mu = 0.3$ M (Li_2SO_4); $[Fe(TMP)_3{}^{3+}]_0 \approx 2.0 \times 10^{-5}$ M; 25.0 °C. [b] Equation 2. [c] $[Na_4P_2O_7] = 1.0 \times 10^{-3}$ M.

Table III. Kinetics Results for the Reaction of $[Fe(TMP)_3]^{2+}$ with HNO_2

$[HNO_2]$, M	k_{obsd}, s^{-1}	k_{calcd},[d] s^{-1}
8.0×10^{-2}	90[b]	87
4.0×10^{-2}	24[b]	26
2.0×10^{-2}	7.5[b]	7.4
1.0×10^{-2}	2.1[b]	2.2
4.0×10^{-3}	0.60[b]	0.59
2.0×10^{-3}	0.23[b]	0.19
1.0×10^{-3}	0.11[b]	0.081
5.0×10^{-4}	0.065[b]	0.037
2.0×10^{-2}	48[c]	49
1.0×10^{-2}	24[c]	23
4.0×10^{-3}	7.8[c]	8.3
2.0×10^{-3}	3.2[c]	3.4
1.0×10^{-3}	1.3[c]	1.2
5.0×10^{-4}	0.50[c]	0.37

[a] $\mu = 1.0$ M (H_2SO_4); 25.0 °C; $[Fe(TMP)_3{}^{2+}]_0 \approx 2 \times 10^{-5}$ M. [b] $[NO]_0 = 9.5 \times 10^{-4}$ M. [c] $[NO]_0 \approx 1.0 \times 10^{-5}$ M. [d] Equation 5.

Table IV. Miscellaneous Kinetics Results for the Reaction of $[Fe(TMP)_3]^{2+}$ with HNO_2[a]

$[HNO_2]$, M	$[H^+]$, M	k_{obsd}, s^{-1}	conditions
1.0×10^{-2}	0.50	2.2	added NO
4.0×10^{-3}	0.50	0.60	added NO
1.0×10^{-2}	0.10	3.0	added NO
4.0×10^{-3}	0.10	0.58	added NO
1.0×10^{-2}	0.50	24.8	
4.0×10^{-3}	0.50	7.0	
1.0×10^{-3}	0.50	1.2	
1.0×10^{-2}	0.10	23.7	
2.0×10^{-3}	0.10	3.2	
1.0×10^{-2}	1.0	24.5	O_2 saturated
1.0×10^{-3}	1.0	1.5	O_2 saturated
1.0×10^{-2}	1.0	3.7	premixed HNO_2
1.0×10^{-2}	0.50	2.0	premixed HNO_2
1.0×10^{-2}	0.10	2.6	premixed HNO_2
1.0×10^{-2}	1.0	24.0[b]	$[TMP] = 5 \times 10^{-4}$ M
1.0×10^{-2}	1.0	23.4	$[LiNO_3] = 2.0 \times 10^{-2}$ M

[a] 25.0 °C; $\mu = 1.0$ M (Li_2SO_4); experiments designated as having added NO had $[NO]_0 = 9.5 \times 10^{-4}$ M. [b] Reaction initiated by mixing NO_2^- with Fe/TMP/H^+.

of the pH dependence revealed that the reaction proceeded to completion in solutions that were not too acidic. However, the reaction failed to reach completion below pH 2.0, and there was no detectable reaction at pH <1.0.

Unlike most oxidations of NO_2^- where pseudo-first-order kinetics have been observed[18] when NO_2^- is present in large excess, the reaction of $[Fe(TMP)_3]^{3+}$ with NO_2^- exhibited distinctly non-pseudo-first-order kinetics, with apparent inhibition toward the end of the reaction. A typical example of this behavior is illustrated in Figure 1. The deviations were more severe for lower $[NO_2^-]$. Added $[Fe(TMP)_3]^{2+}$ was found to inhibit the reactions dramatically.

Initially the reactions were carried out at 1.0 M ionic strength. The reactions were then performed at 0.1 M ionic strength, to see if the deviations from pseudo-first-order kinetics were due to precipitation of the $[Fe(TMP)_3]^{2+}$ product. The rates of the reactions were twofold higher at this lower ionic strength, but the deviations from pseudo-first-order kinetics persisted. No precipitation or turbidity could be visually detected even at concentrations of $[Fe(TMP)_3]^{2+}$ approximately 2 orders of magnitude higher than normally used at this ionic strength. The rates and the nature of the kinetics were unaffected by the presence of nitrate, oxygen, pyrophosphate, free ligand (TMP), and Ni^{2+}(aq). Tests for the effects of NO_3^- and TMP were constrained by the insolubility of $[Fe(TMP)_3](NO_3)_2$ and, at higher pH, of TMP. The results of these blank experiments are presented in Table I.

The pseudo-first-order rate constants obtained from the initial portion of the semilog plots showed a good first-order dependence on $[NO_2^-]$ in the nitrite concentration range 4×10^{-4} to 1×10^{-2} M at pH 7. A study of the pH dependence revealed inhibition at low pH. These results are given in Table II. The data in this table were accurately consistent with the rate law

$$k_{obsd} = k_1[N(III)]/(1 + [H^+]/K_a) \qquad (2)$$

where K_a is the acid dissociation constant of nitrous acid. A fit of the data at $\mu = 0.3$ M to eq 2 gives $k_1 = (3.94 \pm 0.09) \times 10^3$ M^{-1} s^{-1} and $K_a = (9.64 \pm 0.86) \times 10^{-4}$ M. This value of K_a is in good agreement with the literature value of $K_a = 1.1 \times 10^{-3}$ M.[17]

$[Fe(TMP)_3]^{2+}$ + HNO_2. Biphasic kinetics were obtained in the range from pH 1 to pH 2 in agreement with the results of Eptstein and co-workers.[9] However in this pH range the first phase, which was the oxidation of $[Fe(TMP)_3]^{2+}$ by nitrous acid, did not go to completion before the second phase, the reduction of the $[Fe(TMP)_3]^{3+}$ that is formed in the first phase, set in. The first phase went only to 70% completion at pH 2. To simplify the analysis of the system, data were collected only in the range pH <1 where the $[Fe(TMP)_3]^{2+}$ was completely consumed. In this range of acidity only the first phase was observed. It is assumed that the stoichiometry for the first phase is given by eq 3.

$$[Fe(TMP)_3]^{2+} + HNO_2 + H^+ \rightleftarrows [Fe(TMP)_3]^{3+} + NO + H_2O \qquad (3)$$

With HNO_2 in large excess, pseudo-first-order kinetics were observed for the disappearance of $[Fe(TMP)_3]^{2+}$. Rate constants, k_{obsd}, were obtained by exponential fits to the data and are presented in Tables III and IV. The reaction did not show any acid dependence in the acidity range $[H^+]$ = 0.1–1.0 M. Likewise in the experiments with added NO, there was no acid dependence. There was also no acid dependence when premixed HNO_2 solutions were used. Experiments were attempted as in some earlier studies[5] with $[H^+] > 1$ M; however, mixing such concentrated solutions proved to be fairly exothermic and resulted in decomposition of the complex. Consequently, studies were limited to $[H^+] \leq 1.0$ M.

The rate dependence on $[HNO_2]$, as shown in Figure 2, was slightly complicated. It was about $[HNO_2]^{1.3}$ in the absence of

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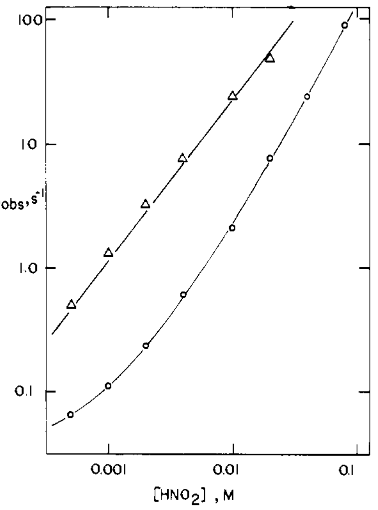

Figure 2. Reaction of $[Fe(TMP)_3]^{2+}$ with nitrous acid: Δ, reactions with no added NO; ○, reactions with [NO] = 9.8×10^{-4} M (data from Table III).

added NO, and in experiments with added NO it varied from $[HNO_2]^{1.0}$ to $[HNO_2]^{1.7}$. Rates obtained with premixed HNO_2 were slower than the rates obtained with HNO_2 generated in situ. Also, the rates obtained with premixed HNO_2 tended to drift to slower values as the solutions aged.

The rate of $[Fe(TMP)_3]^{2+}$ oxidation with HNO_2 was not affected by NO_3^- added at 2×10^{-2} M (above which concentration of NO_3^- the $[Fe(TMP)_3](NO_3)_2$ precipitated) nor by using O_2-saturated solutions or added TMP. In general the rates, insofar as they were comparable, were consistent with those reported by Epstein et al.[9]

Nitric oxide had a strong inhibiting effect on the rate of the reactions. Because of the difficulties in handling NO solutions and because of the low solubility of NO, a study of the dependence on [NO] was not attempted. However, the $[HNO_2]$ dependence with solutions saturated at 0.5 atm partial pressure of NO was studied. The observed rate constants (listed in Table III) were fitted by the two-term rate law

$$k_{obsd} = a[HNO_2] + b[HNO_2]^2 \tag{4}$$

and the values of the parameters obtained are $a = (9.54 \pm 0.85) \times 10^1$ $M^{-1}\,s^{-1}$ and $b = (1.28 \pm 0.02) \times 10^4$ $M^{-2}\,s^{-1}$. The combined data obtained with and without added NO were fitted by eq 5.

$$k_{obsd} = a[HNO_2] - c[NO] + [(c(NO])^2 + d[HNO_2]^2]^{1/2} \tag{5}$$

Since NO is generated both by disproportionation of HNO_2 and by the reaction of $[Fe(TMP)_3]^{2+}$, the concentration of NO in the computer fit was approximated for the reactions without added NO as the mean of the initial and final [NO] (1×10^{-5} M). It was found that the values of c, d, and k_{calcd} were fairly insensitive to the choice of [NO]. The value of the parameters obtained from this fit are $a = (6.6 \pm 2.0) \times 10^1$ $M^{-1}\,s^{-1}$, $c = (2.08 \pm 0.14) \times 10^5$ $M^{-1}\,s^{-1}$, and $d = (6.10 \pm 0.31) \times 10^6$ $M^{-1}\,s^{-1}$. Table IV gives the data for the various blank experiments.

$[Fe(TMP)_3]^{3+}$ + NO. For the $[Fe(TMP)_3]^{3+}$ reaction with nitric oxide the product spectrum had a visible absorption spectrum with λ_{max} and ϵ values corresponding to a (90 ± 10)% yield of $[Fe(TMP)_3]^{2+}$. The reaction is expected to be given by eq 6.

$$[Fe(TMP)_3]^{3+} + NO + H_2O \rightarrow [Fe(TMP)_3]^{2+} + NO_2^- + 2H^+ \tag{6}$$

$[Fe(TMP)_3]^{3+}$ was found to react 20-fold faster with NO than with NO_2^-. Unlike the reactions with NO_2^-, the reactions with NO exhibited perfect pseudo-first-order behavior.

Table V. Kinetics Data for Reaction of $[Fe(TMP)_3]^{3+}$ with NO[a]

pH	k_{obsd}, s^{-1}	pH	k_{obsd}, s^{-1}
7.0[b]	20.5	3.5[d]	6.4
6.0[b]	20.4	1.9[d,e]	5.0
5.0[b]	18.5	1.2[d]	no reaction
4.0[c]	8.2		

[a] μ = 0.3 M (Li_2SO_4); [NO] = 9.5×10^{-4} M, $[Fe(TMP)_3]^{3+} \approx 2.0 \times 10^{-5}$ M. [b] 1.0×10^{-3} M $[P_2O_7^{4-}]$. [c] 1.0×10^{-3} M [phthalate]. [d] Bisulfate buffer. [e] Reaction only 80% completion.

Table VI. Aqueous Equilibrium Data

reaction	value	ref.
$HNO_2 \rightleftarrows H^+ + NO_2^-$	$K_a = 1.1 \times 10^{-3}$ M	17
$NO_2 + e^- \rightleftarrows NO_2^-$	$E° = 0.993$ V	19, 20
$[Fe(TMP)_3]^{3+} + e^- \rightleftarrows [Fe(TMP)_3]^{2+}$	$E_f = 0.84$ V (0.1 M Li_2SO_4)	21
$NO_2(g) \rightleftarrows NO_2(aq)$	$H = 7.0 \times 10^{-3}$ M atm^{-1}	20
$NO(g) \rightleftarrows NO(aq)$	$H = 1.9 \times 10^{-3}$ M atm^{-1}	14
$2HNO_2 \rightleftarrows NO + NO_2 + H_2O$	$K_3 = 6.1 \times 10^{-6}$	19, 20, 14
$HNO_2 + H^+ + e^- \rightleftarrows NO + H_2O$	$E° = 0.875$ V	19, 14
$2NO_2 + H_2O \rightleftarrows HNO_2 + NO_3^- + H^+$	$K_2 = 4.6 \times 10^8$ M	19, 14

The reaction order in [NO] was not studied because of the difficulties in handling dilute solutions of NO; however, the reaction did show a weak acid dependence, and these data are presented in Table V. The primary significance of these results is that they show that the reaction of NO with $[Fe(TMP)_3]^{3+}$ does not occur at low pH; thus this reaction was not a complication in the studies of the reaction of $[Fe(TMP)_3]^{2+}$ with nitrous acid.

Discussion

There are several important equilibria that are useful in discussing the mechanisms of reactions described herein. Due to the recent publication of the revised NBS tables of thermodynamic data[19] and a new value for the solubility for NO_2,[20] it has been necessary to revise the equilibrium constants. The new values are substantially different from the prior values,[9] and these differences have been crucial in attaining a self-consistent interpretation of the kinetics. In order to simplify the discussion, all equilibria and rate constants have been expressed in terms of 1 M aqueous standard states for NO and NO_2. The new results are listed in Table VI.

$[Fe(TMP)_3]^{3+}$ + NO_2^-. The mechanism proposed for the oxidation of NO_2^- by $[Fe(TMP)_3]^{3+}$ is shown in Scheme I.

Scheme I

$$HNO_2 \rightleftarrows H^+ + NO_2^- \quad K_a \tag{7}$$

$$[Fe(TMP)_3]^{3+} + NO_2^- \rightleftarrows [Fe(TMP)_3]^{2+} + NO_2 \quad k_1, k_{-1}, K_1 \tag{8}$$

$$2NO_2 + H_2O \rightarrow HNO_2 + NO_3^- + H^+ \quad k_2 \tag{9}$$

The observed stoichiometry of eq 1 is consistent with this mechanism. Rate law 2, which was obtained from initial rates, can be derived from this mechanism under the approximation that k_{-1} can be neglected. The lower reaction rates observed at μ = 3.0 M compared to the rates at μ = 0.3 M are typical of reactions of ions of opposite charges. Inhibition by added $[Fe(TMP)_3]^{2+}$ and non-pseudo-first-order kinetics are qualitatively consistent with the proposed mechanism.

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(19) Wagman, D. D., et al. *J. Phys. Chem. Ref. Data* **1982**, *11*, Suppl. No. 2. By using the older data of NBS Technical Note #270-3, the following data can be calculated: $E° = 1.045$ V for NO_2/NO_2^-, $K_3 = 1.1 \times 10^{-7}$, $E° = 0.824$ V for HNO_2/NO, and $K_2 = 9.7 \times 10^9$ M. These data lead to a value of 1.2×10^7 $M^{-1}\,s^{-1}$ for k_{-1} from the reaction of NO_2^- with $[Fe(TMP)_3]^{3+}$; on the other hand from the reaction of HNO_2 with $[Fe(TMP)_3]^{2+}$ a value of 2.2×10^8 $M^{-1}\,s^{-1}$ for k_{-1} can be calculated. **Note Added in Proof**: Current studies on the reaction of $IrCl_6^{2-}$ with N(III) appear to support the older NBS data. There are at least three possible sources of error, each of which could contribute a factor of 2 to reconcile the $[Fe(TMP)_3]^{2+}$/N(III) results with the older NBS data: (1) $E° \neq E_f$ for the NO_2/NO_2^- couple. (2) The solubility of NO_2 may really be only 2×10^{-2} $M^{-1}\,atm^{-1}$. (3) There may be a parallel path involving the reaction of $[Fe(TMP)_3]^{2+}$ with N_2O_3; this would augment rate law 21 with the term $e[HNO_2]^2[Fe(TMP)_3^{2+}]$. A least-squares fit of this rate law gives $a = 74.9 \pm 18.6$, $c = (2.5 \pm 0.4) \times 10^5$, $d = (6.0 \pm 0.1) \times 10^6$, and $e = (1.88 \pm 1.13) \times 10^3$.

(20) Lee, Y. N.; Schwartz, S. E. *J. Phys. Chem.* **1981**, *85*, 840.

Disproportionation of NO_2 is favored in preference to further oxidation of NO_2 by $[Fe(TMP)_3]^{3+}$ because generation of NO_2^+ is thermodynamically highly unfavorable[22] and hence it should be a slow process.

By analogy with the observations of Nord and co-workers[23] regarding the oxidation of water by $[Fe(phen)_3]^{3+}$ an alternative mechanism may be applicable in aged solutions (Scheme II). Here Fe^{III}(aquo) simply indicates some degree of hydrolysis. This pathway is not consistent with the observation of non-pseudo-first-order behavior obtained in the presence of added Ni^{2+} to scavenge TMP or $P_2O_7^{4-}$ to tie up Fe^{III}(aquo) or with inhibition by added $[Fe(TMP)_3]^{2+}$. It is clear that, in this case, the hydrolysis mechanism can be rejected in favor of direct reaction of $[Fe(TMP)_3]^{3+}$.

Scheme II

$$[Fe(TMP)_3]^{3+} \rightarrow Fe^{III}(aquo) + TMP \qquad (10)$$

$$Fe^{III}(aquo) + NO_2^- \rightarrow Fe^{II}(aquo) + NO_2 \qquad (11)$$

$$Fe^{II}aquo + TMP \rightarrow [Fe(TMP)_3]^{2+} \quad (fast) \qquad (12)$$

A more detailed treatment of the deviations from pseudo-first-order kinetics may be pursued by evaluating the equilibrium constant for the k_1 step. The pertinent reduction potentials in Table VI lead to $K_1 = 2.6 \times 10^{-3} = k_1/k_{-1}$, and thus $k_{-1} = 1.5 \times 10^6$ M^{-1} s^{-1} can be evaluated. The second-order hydrolysis of NO_2 has been reported to have a rate constant of 1.0×10^8 M^{-1} s^{-1},[20] although a value 50% slower has been reported.[24]

With these rate constants in hand, kinetics curves were simulated by using a simple fourth-order Runga–Kutta integration routine. Some difficulty was encountered because this system of differential equations is mildly stiff, but integrations were obtained under the conditions $[H^+] = 1.0$ M, $[HNO_2] = 1.0 \times 10^{-2}$ M, $[Fe(TMP)_3^{3+}]_0 = 1.1 \times 10^{-5}$ M, and $[Fe(TMP)_3^{2+}]_0 = 4.7 \times 10^{-5}$ M. It was found that the experimental results were accurately simulated when a value of $k_{-1} = 3 \times 10^6$ M^{-1} s^{-1} was used. Considering the uncertainties in the $E°$ values and in the k_2 value, the ability of the simulation to reproduce the inhibitory effect of added $[Fe(TMP)_3]^{2+}$ is quite persuasive.

These results are thus evidence that the fate of the free radical intermediate in this system is disproportionation rather than subsequent electron transfer as is so often seen, e.g., O_2^-, I, SCN, and $S_2O_3^-$.[7,18] The reason for the difference is that in these other systems the radicals rapidly form adducts with bulk species in solution, to form HO_2, I_2^-, $(SCN)_2^-$, and $(S_2O_3)_2^{3-}$, and it is these species that undergo the next electron transfer. In the case of NO_2 there are no such stabilizing pathways.

$[Fe(TMP)_3]^{2+}$ + HNO_2. The decomposition of nitrous acid has been studied by Abel and Schmid[25] and reviewed by Bray.[26] Organic reactions that take place through NO^+ in nitrous acid have been reviewed by Ridd.[1] Stedman in his account of inorganic nitrogen compounds has discussed inorganic reactions of various species in nitrous acid,[2] and Beck and co-workers have reviewed the redox reactions of N(III).[3] Our results lead us to suggest that outer-sphere electron-transfer reactions in nitrous acid have largely been misunderstood.

In the current analysis there are several species present in nitrous acid, which are capable of oxidizing $[Fe(TMP)_3]^{2+}$. NO^+ has been considered to be the most reactive of these,[1,4,5,27,28] and pathways through NO^+ are indicated by rate laws of the form

$$\text{rate} = k[H^+][HNO_2][\text{substrate}] \qquad (13)$$

This rate law can be ruled out in the current investigation, since there was no detectable acid dependence. Two species in solutions of nitrous acid that will not show an acid dependence in their reactions are HNO_2 and N_2O_3. Reaction pathways through these species have been postulated.[9,29] The observed rate suppression with nitric oxide is inconsistent with reactions through these species. A pathway through N_2O_4 can also be pH independent, but this intermediate should give a fourth-order dependence on $[HNO_2]$.

A reaction through NO_2 can show the observed dependence on $[H^+]$, [NO], and $[HNO_2]$. Accordingly, the mechanism proposed for the oxidation of $[Fe(TMP)_3]^{2+}$ in nitrous acid is given by the sequence (14)–(18) (Scheme III).

Scheme III

$$2HNO_2 \rightleftarrows NO + NO_2 + H_2O \quad k_3, k_{-3}, K_3 \qquad (14)$$

$$2NO_2 + H_2O \rightleftarrows HNO_2 + NO_3^- + H^+ \quad k_2, k_{-2}, K_2 \qquad (15)$$

$$[Fe(TMP)_3]^{2+} + NO_2 \rightarrow [Fe(TMP)_3]^{3+} + NO_2^- \quad k_{-1} \qquad (16)$$

$$[Fe(TMP)_3]^{2+} + HNO_2 \rightarrow [Fe(TMP)_3]^{3+} + HNO_2^- \quad k_{HNO_2} \qquad (17)$$

$$H^+ + HNO_2^- \rightarrow NO + H_2O \quad (fast) \qquad (18)$$

Under the conditions that equilibrium K_3 is established rapidly and that k_2 and k_{-2} may be neglected the following rate law can be derived:

$$\frac{-d[Fe(TMP)_3^{2+}]}{dt} = \left\{ k_{HNO_2} + \frac{k_{-1}K_3[HNO_2]}{[NO]} \right\} [HNO_2][Fe(TMP)_3^{2+}] \qquad (19)$$

A value for k_{-3} can be obtained from the pulse radiolytic study of Gratzel et al.[30] They were able to obtain rate constants for the system

$$NO + NO_2 \rightleftarrows N_2O_3 \rightarrow 2HNO_2 \qquad (20)$$

If the reaction is treated as a rapid equilibrium followed by rate-limiting hydrolysis of N_2O_3, their data yield $k_{-3} = 7.0 \times 10^6$ M^{-1} s^{-1}. By combining k_{-3} with K_3 (Table VI) we obtain $k_3 = 42.7$ M^{-1} s^{-1}. Stedman and co-workers[31] have obtained a value indirectly for k_3 of 14 M^{-1} s^{-1} by measurement of the reaction of $S_2O_3^{2-}$ with nitrous acid, and by measurement of oxygen exchange in nitrous acid they have also obtained a value of 5.8 M^{-1} s^{-1} for k_3; we prefer the more direct measurements of Gratzel et al.[30] With this value of k_{-3} and the value of k_{-1}, obtained above, it is easily shown that the condition that K_3 be established rapidly has been met.

The fact that NO_3^- had no effect on the kinetics in the absence of added NO (where a NO_3^- effect should be most significant) is evidence the k_{-2} can be neglected. This can be justified by comparing the predicted rates for the k_{-2} and k_{-1} reactions. The rate constant k_{-1} is known from the reaction of NO_2^- with $[Fe(TMP)_3]^{3+}$ as described above. A value for k_{-2} of 2.7×10^{-2} M^{-2} s^{-1} has also been reported.[2,26] With these rate constants in hand, it is clear that the effects of the k_{-2} path will become important only at unattainably high concentrations of NO_3^-. For slow reactions such as that of Pu(III), however, the effect of NO_3^- is very important.[32]

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High concentrations of NO suppress the concentration of NO_2 and thus reduce the effects of k_2. The fit of eq 4 was obtained for experiments with added NO, where eq 19 is a fair approximation, and so the parameters can be identified as $a = k_{HNO_2}$ and $b = k_{-1}K_3/[NO]$.

Acid dependence studies were carried out under conditions where the k_{HNO_2} term is dominant. Since the rates were independent of $[H^+]$, the k_{HNO_2} term cannot be due to a pathway through NO^+. Formation of HNO_2^- by the reaction of NO_2^- with e_{aq}^- plus H^+, followed by hydrolysis of HNO_2^- as in eq 18, has been observed by Gratzel and co-workers.[24] The gentler reducing agents Fe^{2+}(aq) and Cr^{2+}(aq) have also been reported to react with a pathway involving direct reduction of HNO_2.[27,33] Our value for k_{HNO_2} of 95 $M^{-1}\ s^{-1}$ is greater than that for Fe^{2+}(aq), but this may be due to the greater self-exchange rate of $[Fe(TMP)_3]^{2+/3+}$.

The term second-order in $[HNO_2]$ in eq 4 corresponds to reaction of $[Fe(TMP)_3]^{2+}$ with NO_2. The constant b in eq 4 is $K_3k_{-1}/[NO]$ from which k_{-1} can be obtained as $2.0 \times 10^6\ M^{-1}\ s^{-1}$. This value for k_{-1} is in excellent agreement with the value of $1.5 \times 10^6\ M^{-1}\ s^{-1}$ which was independently obtained by analysis of the reaction of $[Fe(TMP)_3]^{3+}$ with NO_2^-.

Without added NO, it is not appropriate to neglect k_2. k_2 can be included in the rate law by applying the steady-state approximation for $[NO_2]$ in the mechanism (14)–(18). Under the good approximation that k_{-1} can be neglected in the steady-state expression for $[NO_2]$, the following rate law can be derived:

$$\frac{-d[Fe(TMP)_3{}^{2+}]}{dt} = \{a[HNO_2] - c[NO] + [(c[NO])^2 + d[HNO_2]^2]^{1/2}\}[Fe(TMP)_3{}^{2+}] \quad (21)$$

Here the parameters are defined as $a = k_{HNO_2}$, $c = k_{-3}k_{-1}/4k_2$ and $d = k_3k_{-1}{}^2/2k_2$. The values for k_{HNO_2} obtained in the two fits are in reasonable agreement. With these identities, $d/c = 2k_3k_{-1}/k_{-3} = 2K_3k_{-1}$, and with use of the thermochemical value for K_3, it is found that $k_{-1} = 2.4 \times 10^6\ M^{-1}\ s^{-1}$. This value is in good agreement with the value obtained from the experiments only with added NO ($2.0 \times 10^6\ M^{-1}\ s^{-1}$) and the value calculated from the reaction of $[Fe(TMP)_3]^{3+}$ with NO_2^- ($1.5 \times 10^6\ M^{-1}\ s^{-1}$).

The ratio k_{-3}/k_2 is then given by $8c^2K_3/d = 0.35$. The recent value for k_2 of $1.0 \times 10^8\ M^{-1}\ s^{-1}$ [20] and Gratzel's value for k_{-3}[30] lead to an independent measure for k_{-3}/k_2 of 0.07. There are several possible explanations for the fivefold discrepancy between the two determinations of k_{-3}/k_2. One is that the 50% lower value for k_2 obtained by Gratzel and co-workers is actually correct.[24] This would also improve the numerical simulation for the reaction of NO_2^- with $[Fe(TMP)_3]^{3+}$. Another point to note is that although the ratio d/c is quite well-defined, the individual values of c and d are highly correlated. The rough agreement of the two measures of k_{-3}/k_2 is taken as support of the proposed mechanism.

The k_{HNO_2} path was detected in the series with added NO. Without added NO, this path should be most prominent at low $[HNO_2]$. However, the value of k_{HNO_2} predicts that even at $[HNO_2] = 5 \times 10^{-4}$ M this path will contribute only 10% of k_{obsd}. Thus this pathway can nearly be ignored in reactions without the added NO. Epstein et al. reported the same term in their studies,[9] but their value of k_{HNO_2} (approximately eightfold greater than ours) is clearly an artifact which is due to neglect of the effects of NO. Their rate constant for a term first order in $[NO_2^-]$, although now dubious, cannot be tested with our data since we have avoided solutions of low acidity.

Our model can also qualitatively explain the biphasic kinetics observed by Epstein et al. for the reaction of $[Fe(TMP)_3]^{2+}$ with nitrous acid.[9] The reaction in eq 3 goes to completion for pH <1 at all attainable [NO]. For pH >1 it attains an equilibrium position that is controlled by [NO]. As NO_2 slowly hydrolyses, NO is produced by K_3. After eq 3 reaches equilibrium, the position of the equilibrium evolves back toward $[Fe(TMP)_3]^{2+}$ due to the build up of [NO]. This mechanism also explains the lower rates and aging effects obtained with premixed HNO_2 solutions. Disproportionation of HNO_2 produces NO that reduces the concentration of NO_2; consequently $[Fe(TMP)_3]^{2+}$ is oxidized at a lower rate.

There are a few reports of oxidations of metal ions by nitrous acid in which NO_2 is the reactive species.[27,32,34] The reaction of Fe^{2+} with HNO_2[27] was reported to have a term in the rate law that was second order in $[HNO_2]$ and inverse in [NO]. It is difficult to be certain of these results because of an apparent failure to maintain constant ionic strength. Pu(III)[32] and Pu(V)[34] reactions with HNO_2 have been performed under more reliable conditions. The rate law for the Pu(III) reaction with HNO_2 was given as

$$\frac{-d[Pu(III)]}{dt} = k_1[Pu(III)][HNO_2]^{0.5}[H^+]^{0.5}[NO_3^-]^{0.4} \quad (22)$$

and the following mechanism was assigned:

$$HNO_2 + H^+ + NO_3^- \rightleftarrows 2NO_2 + H_2O \quad (23)$$

$$Pu(III) + NO_2 \rightleftarrows Pu(IV) + NO_2^- \quad (24)$$

Similar results were obtained for the Pu(V) reaction. The plutonium reactions differ from that of $[Fe(TMP)_3]^{2+}$ because in the slower plutonium reactions the concentration of NO_2 is governed by the concentration of NO_3^-. These examples serve to demonstrate some degree of precedence for our proposed mechanism.

$[Fe(TMP)_3]^{3+}$ + NO. Many reactions of nitric oxide in aqueous solution with coordinated metal complexes are those in which nitrosyl complexes are formed as simple adducts as in various carboxylate complexes of Fe(II).[35-38] However, redox reactions of NO with coordination complexes in aqueous solution are rare, and to our knowledge, the only examples involve reduction to N_2O.[36] $[Fe(TMP)_3]^{3+}$ is reduced by NO. Assuming the stoichiometry and rate law to be given by eq 25 and 26, the value

$$[Fe(TMP)_3]^{3+} + NO + H_2O \rightleftarrows [Fe(TMP)_3]^{2+} + HNO_2 + H^+ \quad k_4, k_{-4}, K_4 \quad (25)$$

$$d[Fe(TMP)_3{}^{2+}]/dt = k_4[Fe(TMP)_3{}^{3+}][NO] \quad (26)$$

of k_4 can be calculated as $2.0 \times 10^4\ M^{-1}\ s^{-1}$. The apparent pH dependence is not understood. A value for K_4 of 0.38 M can be calculated from the pertinent $E°$ values as listed in Table VI. Since $K_4 = k_4/k_{-4}$, the experimental rate of reaction of NO with $[Fe(TMP)_3]^{3+}$ implies a value for k_{-4} of $5.3 \times 10^4\ M^{-2}\ s^{-1}$. This calculated value far exceeds the diffusion-controlled rate constant for NO^+ ($5 \times 10^2\ M^{-2}\ s^{-1}$)[1,5,39] with an ion of this charge and size. A third-order rate constant of $5.3 \times 10^4\ M^{-2}\ s^{-1}$ should have been observable in our experiments. The pH-dependent experiments at low $[HNO_2]$ with added NO suggest an upper limit of $1.5 \times 10^2\ M^{-2}\ s^{-1}$ for k_{-4}. For these reasons the reaction of NO with $[Fe(TMP)_3]^{3+}$ appears not to proceed through NO^+. Since neither the order in [NO] nor the nitrogen products have been determined, further speculation on the mechanism of this reaction is unwarranted.

NO_2/NO_2^- Pathways. Discussions of the factors controlling the rates of outer-sphere electron-transfer reactions involving the NO_2/NO_2^- couple have been presented previously.[6,18] Some revision of these considerations is dictated by the results of the current investigation. Two specific changes need to be incorporated; one is the new reduction potential for the NO_2/NO_2^- couple, and the other is the observation that although there is a stoi-

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Table VII. Marcus–Hush Calculations for the NO_2/NO_2^- Couple[a]

oxidant	$E°$, V	k_1, $M^{-1}\ s^{-1}$	k_{22}, $M^{-1}\ s^{-1}$	r, Å	k_{11}, $M^{-1}\ s^{-1}$
$[Fe(TMP)_3]^{3+}$	0.84	3.8×10^3	5×10^9	6.5	9.7×10^{-2}
$[Fe(bpy)_3]^{3+}$	1.06	6.5×10^4	5×10^8	6.0	2.5×10^{-2}
$Fe(CN)_6^{3-}$	0.34	2.1×10^{-5}	5×10^3	4.5	1.2×10^{-2}
$IrCl_6^{2-}$	0.892	1.96×10^1	2×10^5	4.4	2.8×10^{-2}
$IrBr_6^{2-}$	0.843	5.7×10^1	2×10^8	4.7	2.1×10^{-3}

[a] Data taken from ref 18 except for the reaction of $[Fe(TMP)_3]^{3+}$ where the data are discussed in this paper. Radii are only crude estimates. k_{11} values calculated by using the Marcus–Hush cross relationship as in ref 6, assuming a radius for NO_2 of 1.9 Å.

chiometric factor of 2 in the net oxidation of NO_2^- to NO_3^-, this factor should not appear in the rate laws for these reactions because the fate of NO_2 is disproportionation, not subsequent oxidation. As before, the rate constants can be compared by using the cross relationship of Marcus–Hush theory to calculate an effective self-exchange rate constant, k_{11}, for the NO_2/NO_2^- couple. The results of these calculations are displayed in Table VII. The self-exchange rate constant k_{22} for the $[Fe(TMP)_3]^{3+/2+}$ couple has not been measured in aqueous solution; in acetonitrile it was found to be fivefold faster than for the $[Fe(bpy)_3]^{3+/2+}$ couple, but these results were quite sensitive to the nature of the counterion.[40] For the calculations in Table VII, k_{22} has arbitrarily been set at $5 \times 10^9\ M^{-1}\ s^{-1}$. The calculated values are scattered within a factor of 48, with k_{11} calculated from the $[Fe(TMP)_3]^{3+}$ reaction being largest. This degree of scatter is probably acceptable considering the gross difference in size between the reactants. The results actually are very similar to those previously reported;[6,18] this has occurred due to a fortuitous cancellation of effects. Thus, the prior treatment of the self-exchange process in terms of solvation, Franck–Condon factors, and nuclear tunneling remains unaffected.[6]

It is of interest to consider some published results on the reaction of $Fe(CN)_6^{4-}$ with nitrous acid.[4] The reaction was found to be acid dependent, but it reached a limiting rate at high acidities. This was attributed to the reaction of NO^+ with $HFe(CN)_6^{3-}$. The effects of added NO were not investigated. A reaction through NO_2 and $H_2Fe(CN)_6^{2-}$ would also be independent of pH at high acidities. The reaction of NO_2 with $Fe(CN)_6^{4-}$ has been measured by pulse radiolysis.[41] If the reactivity of $H_2Fe(CN)_6^{2-}$ is not too much greater than $Fe(CN)_6^{4-}$, then one may speculate that, in the reaction of ferrocyanide with nitrous acid, NO_2 rather than NO^+ carries the reaction.

NO/NO^+ Pathways. One of the objectives in carrying out this investigation was to learn more about outer-sphere electron-transfer reactions involving the NO/NO^+ redox couple. We have found that the direct oxidation of NO by $[Fe(TMP)_3]^{3+}$ apparently does not involve formation of NO^+, and in the oxidation of $[Fe(TMP)_3]^{2+}$ by nitrous acid, NO^+ plays no detectable role. Furthermore, we have proposed that the oxidation of $Fe(CN)_6^{4-}$ by nitrous acid does not proceed via NO^+. The evidence in favor of such a pathway for the reaction of $Fe^{2+}(aq)$ is quite slender.[27] A path through NO^+ was proposed for the reactions of $[Fe(phen)_2(CN)_2]$ and $[Fe(bpy)_2(CN)_2]$ with nitrous acid; however, the effects of NO were not investigated, and a complex acidity dependence was uncovered.[5] In summary, there appears to be little convincing evidence in favor of reaction through a NO^+ pathway in outer-sphere reactions.

Predominance of NO_2 over NO^+ pathways in outer-sphere reactions is not thoroughly unexpected. Eberson and Radner[42] have estimated that the reorganizational energies for the NO_2/NO_2^- and NO/NO^+ couples are very similar ($\lambda \approx 70$ kcal/mol^{-1}). A simple calculation by using the Marcus–Hush cross relationship predicts that NO_2 pathways should at least be competitive with NO^+ pathways, since the higher $E°$ for NO^+ is offset by the difficulty in generating NO^+. The prevalence of NO^+ pathways in more conventional nitrosation reactions is due, not to the greatly enhanced reactivity of NO^+, but rather to the diminished reactivity of NO_2.

Conclusions. Reinvestigation of the biphasic reaction of $[Fe(TMP)_3]^{2+}$ in nitrous acid has uncovered a different rate law. Since NO has a strong retarding effect, the mechanism has been reinterpreted as proceeding through disproportionation of HNO_2 to form NO_2 and NO, followed by rate-limiting reduction of NO_2 by $[Fe(TMP)_3]^{2+}$. The second phase is due to irreversible formation of NO_3^-. The central role played by the NO_2/NO_2^- couple has been confirmed by direct measurement of the oxidation of NO_2^- by $[Fe(TMP)_3]^{3+}$. Failure to observe a pathway through NO^+ has been proposed to be a common phenomenon for outer-sphere electron-transfer reactions in nitrous acid.

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Registry No. HNO_2, 7782-77-6; $[Fe(TMP)_3]^{3+}$, 17378-81-3; $[Fe(TMP)_3]^{2+}$, 17378-70-0.

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