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The Catalytic Reduction of Nitrite. Metal Coordination and Reaction of Nitrosyl with Hydrazine: Two-Electron Oxidants Can Also Lead to Ammonia

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The electrophilic reactions of NO^+ bound to transition metals with ancillary coligands are important within the subject of NO reactivity.[1] The reactions of OH^-, amines, and thiolates are also relevant to modern studies on the physiology of NO dealing with the mechanisms of transport and reactivity upon coordination to iron enzymes.[2] NO binds to many transition metals by forming an electronically delocalized [M−N−O] moiety, with the N-atom being the site either for nucleophilic addition or outer-sphere electron transfer.[3] This is a key condition for the reduction of nitrite, requiring its coordination and proton-assisted dehydration leading to an $Fe^{II}-NO^+$ species in a d^6 system with low-spin configuration.[4] This occurs also for the initial steps in the reactivity of the nitrite reductase enzymes.[5]

We show that nitrite can be catalytically reduced in several steps, starting with coordination to $Fe(CN)_5H_2O^{3-}$, acid−base conversion to $Fe(CN)_5NO^{2-}$ (a well-recognized hypotensive agent)[2,6] and further attack by hydrazine. The nucleophilic reactivity of hydrazine toward NO^+, promoting nitrosation in competition with outer-sphere reductions, has been considered in the studies of dissimilatory nitrite reductases.[5b] Although hydroxilamine,[7] azide,[7] and ammonia[8] were used as nucleophiles with $Fe(CN)_5NO^{2-}$, strikingly, hydrazine was not.[1] The reactivity of hydrazine is interesting in its own right,[9] and the mechanism of its addition reactions to several complexes, as well as to nitrous acid, remains an open subject.[5b,10,11]

We first present a stoichiometric, kinetic, and mechanistic study of the reaction of pentacyanonitrosylferrate(II) with hydrazine. The stoichiometry is described by eq 1

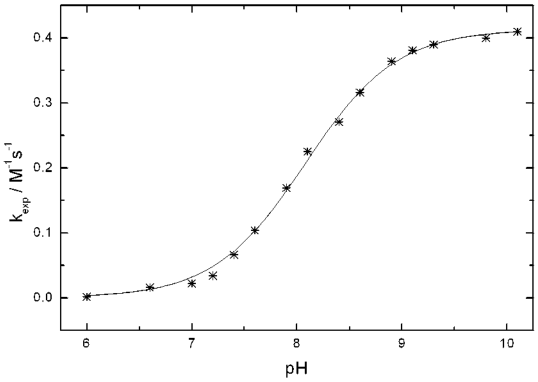

Figure 1. Plot of the second-order rate constant, k_{exp} (M^{-1} s^{-1}) against pH. T = 25.0 °C; I = 1 M (NaCl); $[Fe(CN)_5NO^{2-}] = 1 \times 10^{-4}$ M; $[N_2H_4]_T = 7.5 \times 10^{-3}$ M.

$$Fe(CN)_5NO^{2-} + N_2H_4 + H_2O \rightarrow Fe(CN)_5H_2O^{3-} + N_2O + NH_3 + H^+ \quad (1)$$

The formation of ammonia appears as of high mechanistic significance, as shown below.[9] All yields were checked for eq 1: the $Fe(CN)_5H_2O^{3-}$ ion was quantitatively determined by generating the $Fe^{II}(CN)_5$isonicotinamide^{3-} ion.[12] N_2O and NH_3 were identified by mass spectrometry,[13] and the delivery of H^+ was quantified through a pH-stat titration. Under excess of hydrazine, $Fe(CN)_5N_2H_4{}^{3-}$ is formed.[14] Consumed hydrazine, measured by titration, agrees with eq 1.

The rate law, measured through the buildup of products, $Fe(CN)_5H_2O^{3-}$ and N_2O, was: $v = k_{exp}\,[Fe(CN)_5NO^{2-}]\,[N_2H_4]$. Figure 1 shows the dependence of k_{exp} on pH, according to: $k_{exp} = k_{hydr}/\{1 + [H^+]/K_a\}$, where K_a corresponds to $N_2H_5{}^+ \leftrightarrow N_2H_4 + H^+$, and k_{hydr} relates to the reactivity of N_2H_4.

A very good fit to the rate law was found by taking $pK_a = 8.1$, in agreement with the literature value, 8.0,[9] and $k_{hydr} = 0.40 \pm 0.02$ M^{-1} s^{-1} (25.0 °C); the results also show that $N_2H_5{}^+$ is unreactive. Activation parameters (pH 9.2) were: $\Delta H^{\ddagger} = 26.8 \pm 0.2$ kJ mol^{-1}, $\Delta S^{\ddagger} = -163 \pm 5$ J K^{-1} mol^{-1}.

The results can be included under a general mechanistic framework, operative for the reactions of nitrosyl-complexes with different nucleophiles, B:[1]

$$Fe(CN)_5NO^{2-} + B \leftrightarrow \{Fe(CN)_5NO^{2-}\cdot B\} \rightarrow Fe(CN)_5H_2O^{3-} + \text{redox products} \quad (2)$$

The first reaction can be treated as an equilibrium, followed by irreversible redox rearrangements. The nature of the elementary steps and relative rates are dependent on B; for B = OH^-, unreactive $NO_2{}^-$ is formed, with no redox reactions. Below pH

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11, we discard OH^- as a nucleophilic hydrazine competitor.[15] In reaction 2, either the forward rate of nucleophilic addition, or any elementary step associated to adduct decomposition could be rate-determining. We favor the first assumption, as k_{hydr} and the activation parameters are consistent with the results for other nucleophiles.[7, 15,16]

The adduct can be described as a $\{(NC)_5Fe{-}N(O)NH_2NH_2\}$ species, which rapidly deprotonates at the binding-nitrogen of hydrazine.[17] The stoichiometry requires the migration of the second proton to the remote N-atom of hydrazine, followed by a cleavage of the single N−N bond in hydrazine and delivery of ammonia. The resulting $[Fe(CN)_5N_2O]^{3-}$ is unstable toward dissociation. A strong mechanistic evidence is given by an experiment with labeled $Fe(CN)_5{}^{15}NO^{2-}$:[18] the mass profile shows unequivocally that ^{15}N appears only at the N_2O gas (but *not* at NH_3) and that the label remains at the central N atom, the one bound to O.

The reaction of $[Ru^{II}(NH_3)_5NO]^{3+}$ with hydrazine led to N_2O and N_2, but no ammonia was found;[10a] the *trans*-$[M(pdma)_2Cl(NO)]^{2+}$ (M = Ru,Os; pdma = *o*-phenylenebis(dimethylarsine)) complexes led to azide formation as a bound ligand, with N_2 as byproduct.[10b,c] In the reaction of HNO_2 with $N_2H_5{}^+$, at pH 1, hydrazoic acid, HN_3, was obtained quantitatively.[11] The yield of HN_3 decreased with increasing pH, together with formation of equal amounts of NH_3 and N_2O. Stedman proposed two alternative routes for the decomposition of the nitrosohydrazine intermediates:[11] (a) one leading to $NH_3 + N_2O$ (k_a) and (b) the other to $HN_3 + H_2O$ ($k_b[H^+]$). This explains some confusing results in the literature showing the appearance of complex mixtures of N_2O, NH_3, N_2, and HN_3;[19] further reactivity of azide with NO^+, leading to N_2 and N_2O, must be also considered.[11] The behavior of the Ru and Os complexes could be interpreted on this basis. To our knowledge, this is the first report on rigorously quantitative results for Stedman's prediction of hydrazine nitrosation evolving through the *exclusive* route a.

The different reaction modes of nitrosyl in the Fe, Ru, and Os complexes may depend on the metal and coligands (both influence the NO electron density and thus the reduction potential at the nitrosyl site through the $\sigma-\pi$ interactions).[20] However, after the removal of both protons from the binding N-atom, the overall charge on the electrophile can be determinant: the positive charge of the Ru and Os complexes facilitates proton loss from the terminal nitrogen and water removal, leading to bound azide. With $Fe(CN)_5NO^{2-}$, the protons are retained, and ammonia is released after a heterolytic cleavage of the N−N bond.

Figure 2 shows the catalysis of nitrite reduction, measured by the consumption of hydrazine, under controlled conditions. High quantities of free nitrite can be processed if enough hydrazine is present. pHs around 9−10 and an excess of nitrite over hydrazine favor the catalytic process. The latter (Scheme 1) depends on the lability of the Fe−L bond in the $Fe(CN)_5L^{n-}$ ions (L = H_2O, $NO_2{}^-$, N_2O, N_2H_4), and on the fast conversion of bound nitrite to NO^+. At pH ≥ 11, unreactive N-bound nitrite is predominant. Although hydrazine and ammonia could inhibit the reaction through binding to the iron site, the equilibrium picture favors $Fe^{II}{-}NO^+$ formation. pHs lower than 7 must be avoided, because otherwise the predominant $N_2H_5{}^+$ ion would be unreactive, as stated above.

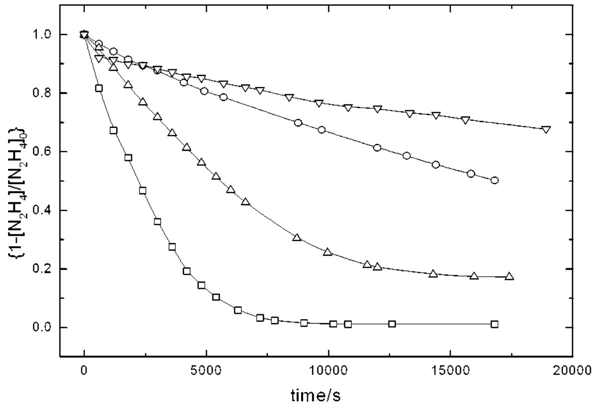
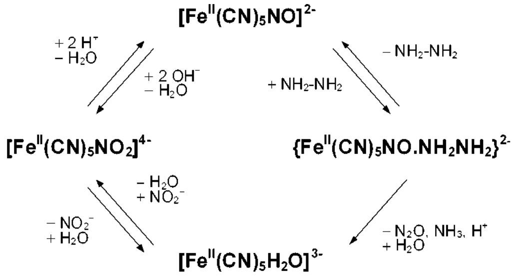


Figure 2. Hydrazine decay vs time in different reaction conditions. T = 25.0 °C; I = 1 M, NaCl; $[N_2H_4]_o = 1.3 \times 10^{-2}$ M; $[Fe(CN)_5H_2O^{3-}] = 1.3 \times 10^{-3}$ M. (▽) pH 9.2; $[NO_2{}^-]$ 0.04 M. (○) pH 7.0; $[NO_2{}^-]$ 0.12 M. (△) pH 10.2; $[NO_2{}^-]$ 0.12 M. (□) pH 9.2; $[NO_2{}^-]$ 0.12 M.

Scheme 1



There is some resemblance between the catalytic behavior of $Fe^{II}(CN)_5H_2O^{3-}$ and the dissimilatory nitrite reductases.[5] The enzyme promotes NO release from the initiallly NO^+-bound complex, but nitrosation reactions of nucleophiles are also catalyzed.[5] We did not focus on the reductive one-electron step leading to NO,[21,22] but we emphasize on a nitrosation reaction that seems to parallel the enzyme behavior.[5b] In reaction 1, hydrazine promotes a two-electron transfer to NO^+, and neither NO nor NO^- intermediates are detected. There is no need of additional reductants, as claimed for the enzyme.[5b] N_2O appears as a unusual product of hydrazine oxidation, which generally leads to dinitrogen.[9] Interestingly, however, we found that 1,2-dimethylhydrazine promotes a one-electron reduction to $Fe^{II}(CN)_5NO^{3-}$.[21] Finally, we show that nitrosation of hydrazine may be a general route to ammonia in hydrazine oxidations. The widely accepted proposal that ammonia production occurs only for one-electron oxidants needs to be modified.[9,23]

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