

Figure SI 1. Pseudo-first order plots of the 440 nm band decay for 1.0×10^{-4} M $[\text{Fe}(\text{CN})_5\text{H}_2\text{O}]^{3-}$; $[\text{NH}_2\text{OH}]$: (□) 5.0×10^{-3} M; (○) 4.0×10^{-3} M; (△) 3.0×10^{-3} M; (▽) 2.0×10^{-3} M, $I = 1$ M NaCl; pH 7 (phosphates), 25 °C.

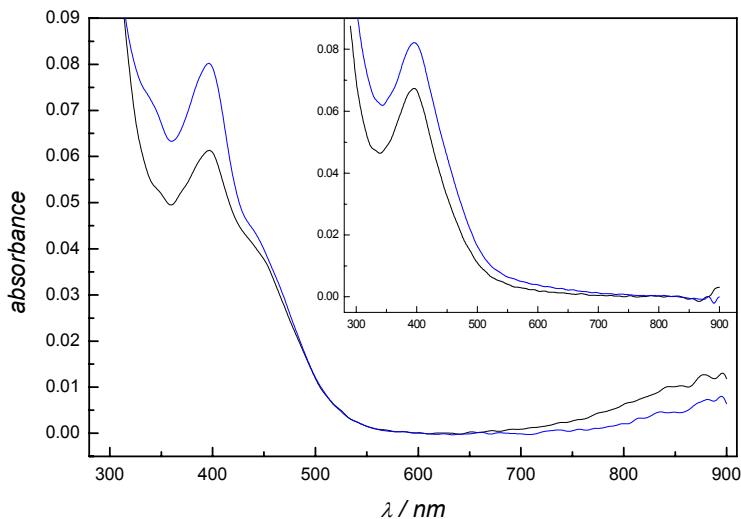


Figure SI 2. In black: UV-vis spectrum obtained during the reaction of $8 \times 10^{-5} \text{ M } [\text{Fe}(\text{CN})_5\text{H}_2\text{O}]^{3-}$ with $8 \times 10^{-5} \text{ M } \text{NH}_2\text{OH}$, pH 7, $I = 1.9 \text{ M}$ (phosphates), $T = 25^\circ\text{C}$. In blue: Spectrum obtained in the reaction of $[\text{Fe}(\text{CN})_5\text{H}_2\text{O}]^{3-}$ with $[\text{O}_2]_{\text{aq}}$, in similar conditions as with NH_2OH . Inset: Same experiments at pH 9.3.

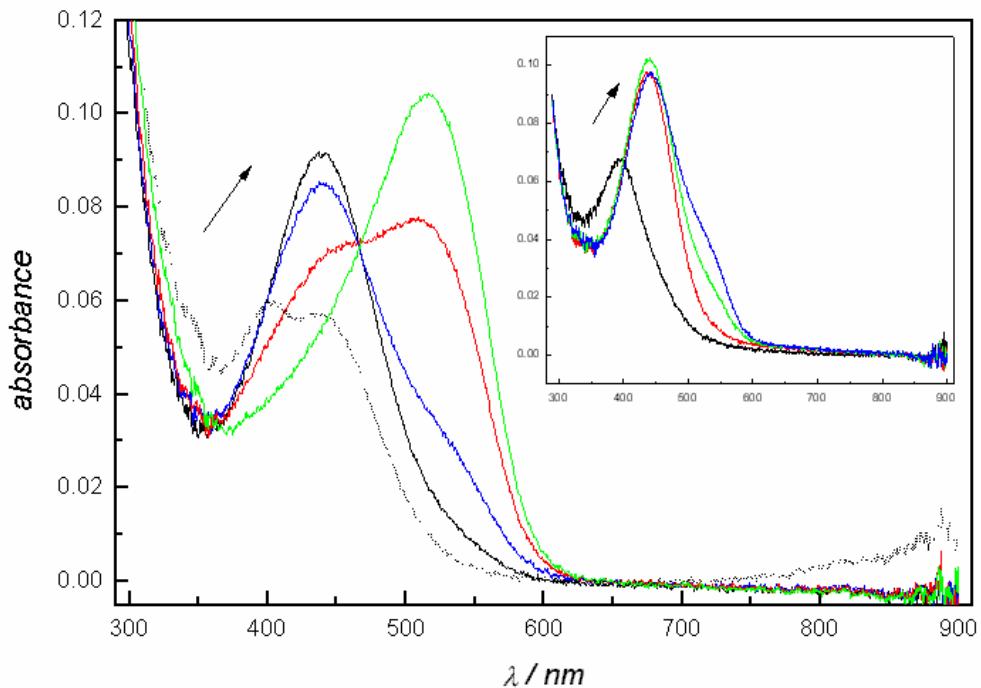


Figure SI 3. Spectral changes associated with the 440-520 nm transformation observed at pH 7 (inset pH 9.3) after the addition of N_2H_4 to the exhausted solutions obtained adding 8×10^{-5} M NH_2OH to 8×10^{-5} M $[\text{Fe}(\text{CN})_5\text{H}_2\text{O}]^{3-}$, $T = 25^\circ\text{C}$.

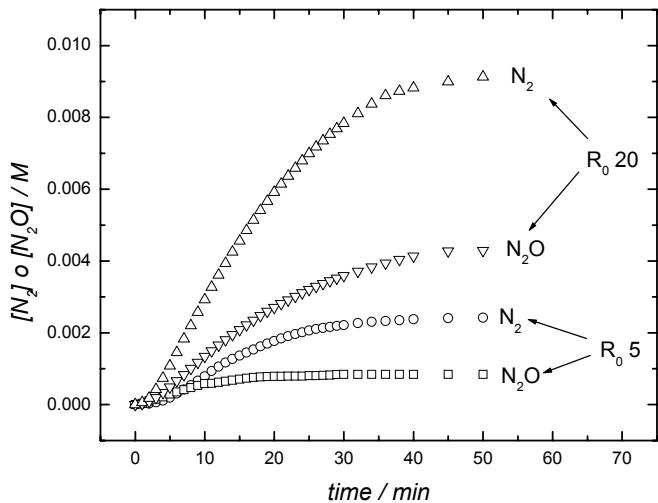


Figure SI 4. Time evolution of the gaseous products observed for the reaction between 2.5×10^{-3} M $[\text{Fe}(\text{CN})_5\text{H}_2\text{O}]^{3-}$ and 1.25×10^{-2} M NH_2OH : $R_0 = 5$, N_2O (\square) $\text{N}_2(\text{O})$. For 5.0×10^{-2} M NH_2OH : $R_0 = 20$, N_2O (∇) N_2 (Δ); pH 6, $I = 1.2$ M (phosphates), $T = 25$ °C. Each curve reflects the accumulation of species in the reactor.

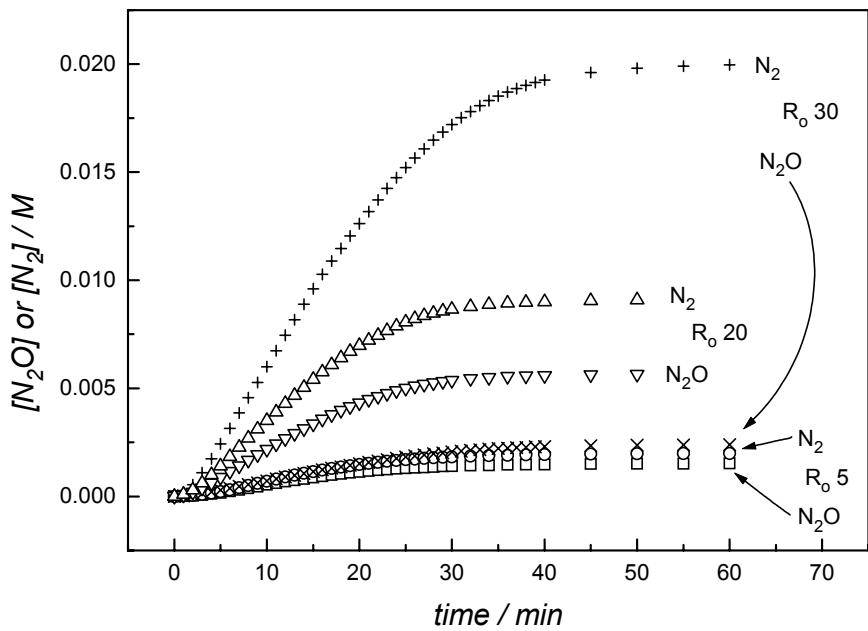
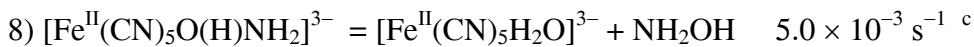
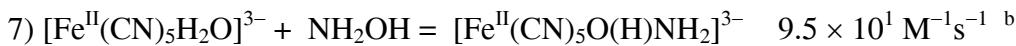
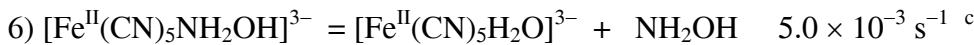
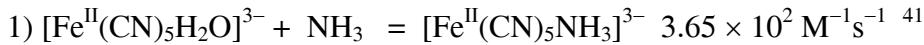


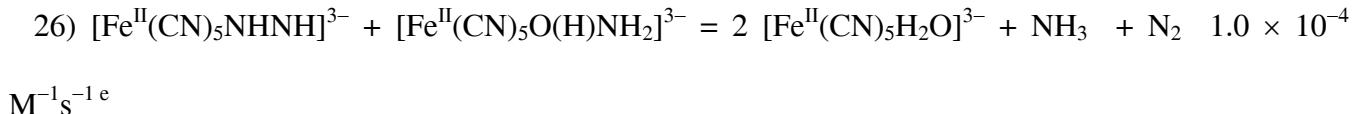
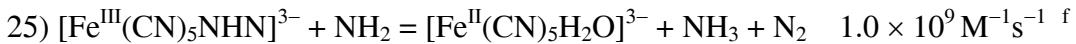
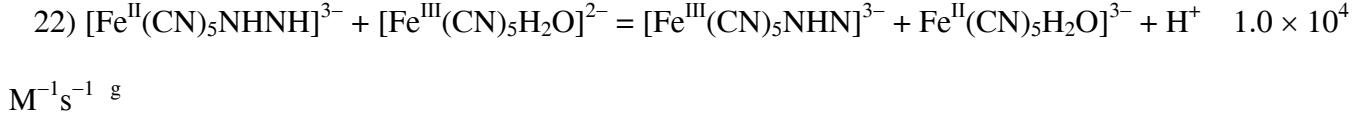
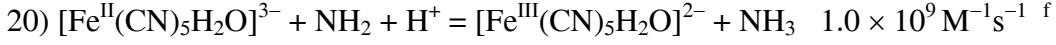
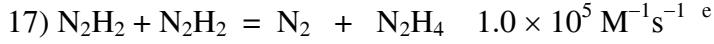
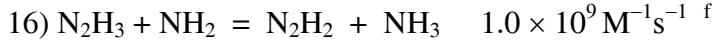
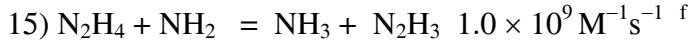
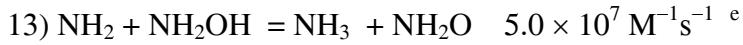
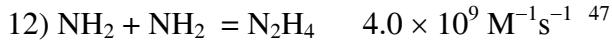
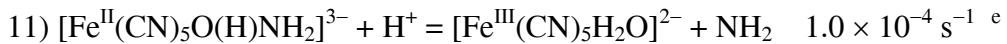
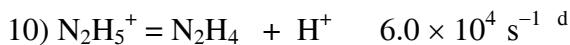
Figure SI 5. Time evolution of the gaseous products observed for the reaction between 2.5×10^{-3} M $[\text{Fe}(\text{CN})_5\text{H}_2\text{O}]^{3-}$ and NH_2OH : 1.25×10^{-2} M, $R_0 = 5$, N_2O (\square) N_2 (\circ); 5.0×10^{-2} M, $R_0 = 20$, N_2O (∇) N_2 (Δ); 7.5×10^{-2} M, $R_0 = 30$, N_2O (\times) N_2 ($+$); pH 8, $I = 2.6$ M (phosphates), $T = 25$ °C. Each curve reflects the accumulation of species in the reactor.

Scheme SI 6. Simulation Procedure.

In the proposed mechanism, rate constants are needed for several steps, namely: 11, 13, 14, etc., which could not be determined in the present work, or are unavailable from the literature. Our goal is not to obtain a good fitting of the parameters, rather the aim is to verify the central hypothesis of the proposed mechanism, i.e.: the change of regime established at high concentrations of NH₂OH is a consequence of the increasing importance of the radical termination reactions, particularly that involving NH₂ against, probably, Fe(II)-N₂H₂. In addition, in order for the calculation to reproduce the experimental observations, we proposed that the main products are generated in the propagation steps when the reaction operates in the fast regime, and that they are formed through the molecular path when the process is under the inhibited regime.

The following are the reactions and associated rate constants that sustain the behavior described in Figures SI 7,8.





The initial concentration of $[\text{Fe}^{\text{II}}(\text{CN})_5\text{NH}_3]^{3-}$ was maintained constant, 2.5×10^{-3} M, and the concentration of NH_2OH was varied between 2.5×10^{-2} M and 2.5×10^{-1} M. The pH-dependent rate constants are considered for pH 7. For all other involved species the initial concentrations were zero.

The sensitivity of the reactions allowed to establish that in the fast regime the consumption of NH_2OH depends mainly on the values of k_7 , k_8 , k_{11} , k_{13} and k_{20} . The production of N_2O and N_2 was found sensitive to k_7 , k_8 , k_{11} , k_{18} , k_{19} , and to k_8 , k_{11} , k_{18} y k_{19} , respectively. For the inhibited regime the consumption of NH_2OH depends on the values of k_6 , k_7 , k_{11} and k_{13} . Finally, the production of $[\text{Fe}^{\text{II}}(\text{CN})_5\text{N}_2\text{H}_2]^{2-}$, which promotes the change of regime, is sensitive to k_5 , k_6 , k_7 , k_8 , k_{11} , k_{13} and k_{21} .

a.- Ruff, F and Csizmadia, I.G., "Organic Reactions. Equilibria, Kinetics and Mechanism. Elsevier, Amsterdam, 1995, p. 398.

b.- Present work. Assuming the same probability for the coordination through N or O, and considering the measured rate constant for the decay at 440 nm, $190 \text{ M}^{-1}\text{s}^{-1}$.

c.- We consider an intermediate value between those measured for NH_3 y N_2H_4 .

d.- Values corresponding to $\text{NH}_3/\text{NH}_4^+$, adequately modified for reproducing a pK_a of 8.0.

e.- Calculation parameters.

f.- Not known. We suppose it sufficiently fast in order that the accumulation of species is avoided.

g.- Estimated value from related reactions. H.E. Toma and J.M. Malin, J.Am.Chem.Soc. 1975, 97, 288.

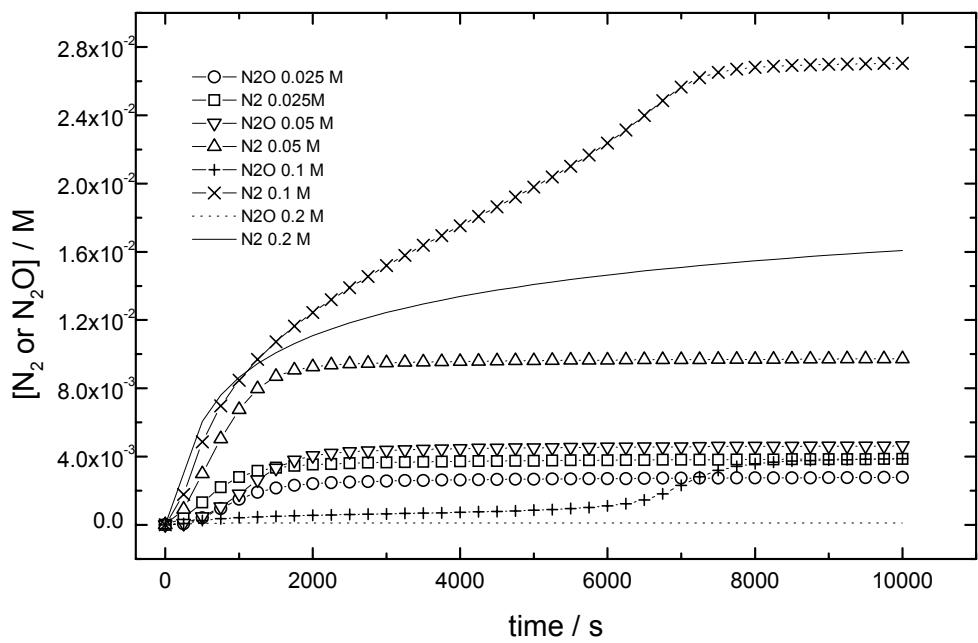


Figure SI 7. Calculated concentrations with $[\text{Fe}^{\text{II}}(\text{CN})_5\text{NH}_3]^{3-}$ 2.5×10^{-3} M and NH_2OH : 0.025 M: (-○-) N_2O , (-□-) N_2 ; 0.05 M: (-▽-) N_2O , (-△-) N_2 ; 0.1 M: (-+-) N_2O , (-×-) N_2 ; 0.2 M: (----) N_2O , (—) N_2 .
 pH = 7.

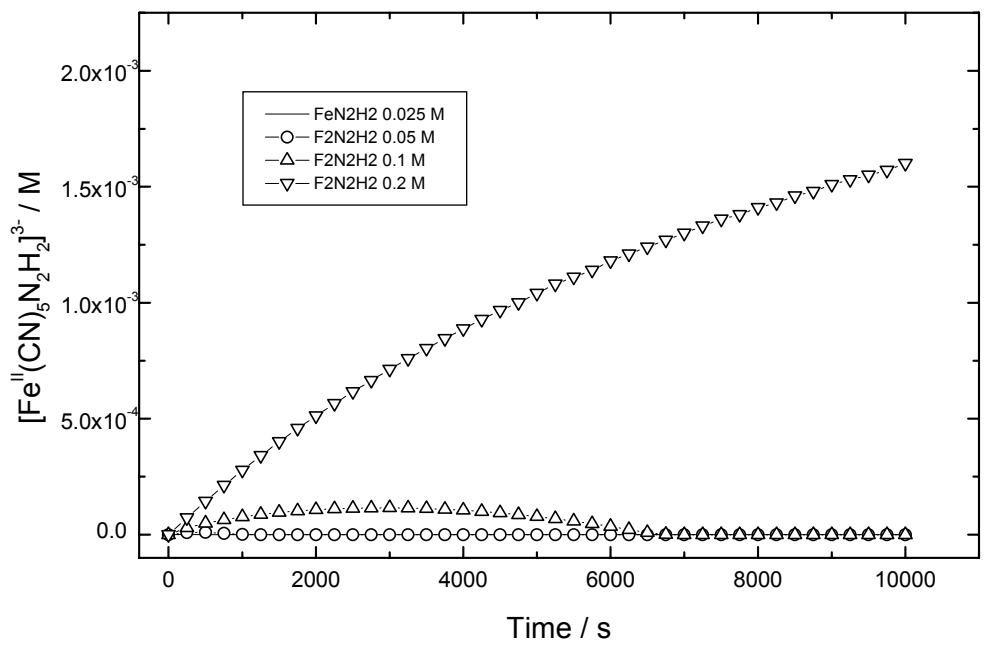


Figure SI 8. Calculated concentration with $[\text{Fe}^{\text{II}}(\text{CN})_5\text{NH}_3]^{3-}$ 2.5×10^{-3} M and NH_2OH : 0.025 M (—); 0.05 M (-O-); 0.1 M (-Δ-); 0.2 M (-∇-). $\text{pH} = 7$.