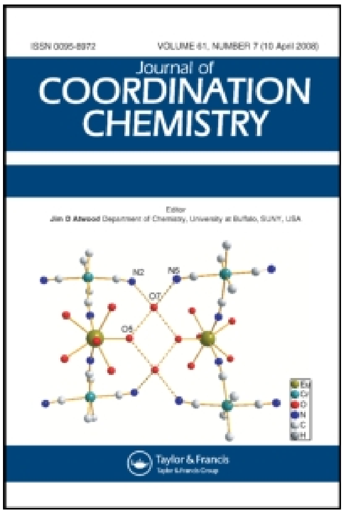

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KINETICS AND MECHANISM OF THE REACTION BETWEEN PENTACYANONITROSYLFERRATE(II) AND HYDROXYLAMINE

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KINETICS AND MECHANISM OF THE REACTION BETWEEN PENTACYANONITROSYLFERRATE(II) AND HYDROXYLAMINE

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The kinetics of the reaction between pentacyanonitrosylferrate(II) and hydroxylamine was studied spectrophotometrically and gas volumetrically in moderately alkaline media (pH = 8 –9.5). Reduction of the nitrosyl ligand takes place according to the following stoichiometry:

$$Fe(CN)_5NO^{2-} + NH_2OH = Fe(CN)_5H_2O^{3-} + N_2O + H^+$$

The aquocomplex catalyses the following two disproportionation reactions of hydroxylamine:

$$4\,NH_2OH = N_2O + 2NH_3 + 2H_2O$$

and

$$3NH_2OH = N_2 + NH_3 + 3H_2O$$

Two paths for disproportionation were identified: a fast route, probably *via* radicals, initiated by a binuclear intermediate yielding N_2 or N_2O and a slower one through formation of $Fe(CN)_5NO^{4-}$ as a stable intermediate yielding N_2. A kinetic model was constructed which describes both the reduction of nitrosyl complex and the catalytic disproportionation reactions of hydroxylamine.

KEYWORDS: nitroprusside, pentacyanonitrosylferrate(II), pentacyanoammineferrate(II), hydroxylamine, catalytic disproportionation

INTRODUCTION

The reactivity of small molecules considerably changes by coordination to a metal center.[1,2] Coordination influences either the thermodynamic properties of the

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ligand, *e.g.* redox potentials, or kinetic behaviour *i.e.* the rate and mechanism of redox reactions. The effects could be dramatic or negligible. Coordination is a fundamental feature of catalysis for a wide range of reactions from enzymatic activity to different industrial processes. The basic reason for the catalytic effect of metal complexes is the enhanced reactivity of ligands on coordination.

Pentacyanonitrosylferrate(II) is one of the best model compounds for studying the effect of coordination on reactivity of a coordinated ligand. It is a thermodynamically stable compound and, in moderately alkaline medium, is inert toward ligand substitution.[3,4] In pentacyanonitrosylferrate(II) the nitrosyl ligand retains its nucleophilic character and takes part in a wide variety of oxidation-reduction reactions. Some of these reactions were discovered a long time ago *e.g.* the Gmelin — reaction with sulphide[4,5] or thiol groups.[6] These colored reactions still have analytical importance. Pentacyanonitrosylferrate(II) is applied to decrease human blood pressure.[7] This effect is attributed to the reaction between coordinated nitrosyl and SH containing essential amino-acids.[8] According to the current opinions pentacyanonitrosylferrate(II) is a NO source in living systems.[9]

In pentacyanonitrosylferrate(II) the coordinated nitrosyl can be reduced to N_2 by a primary amino group containing organic substrates.[10–14] Although the kinetics and the mechanism of these reactions were intensively studied, there are still some problems in the details of this oxidation-reduction reaction involving three electrons. It seems likely that the electron exchange between N(3 +) in the nitrosyl and N(-3) in the amines occurs only in part within the coordination sphere . The formation of N_2 in the last step takes place after the intermediate leaves the coordination sphere.[15] When the substrates are diamines or diamino-acids cyclic imines were found to be the dominant products.[16]

In order to obtain further information on the mechanism of reduction of coordinated nitrosyl, we decided to study in detail the kinetics of reactions between pentacyanonitrosylferrate(II) and different simple reducing agents. The substrates under study are hydroxylamine (N(-1)), hydrazine (N(-2)), glycine and ethylenediamine(N(-3)). In this paper we report on the reaction with hydroxylamine.

There is complete agreement among researchers[17–19] concerning the stoichiometry:

$$Fe(CN)_5NO^{2-} + NH_2OH = Fe(CN)_5H_2O^{3-} + N_2O + H^+ \qquad (1)$$

Based on gas volumetric measurements we found[17] the kinetic order for pentacyanonitrosylferrate(II) to be one, while for hydroxylamine the kinetic order changes between one and two. It is important to note that in this measurement only the initial rate was studied. The following scheme was suggested:

$$Fe(CN)_5NO^{2-} + OH^- \underset{}{\overset{K_2}{\rightleftharpoons}} Fe(CN)_5(NO_2H)^{3-} \qquad (2)$$

$$\begin{aligned} Fe(CN)_5(NO_2H)^{3-} + NH_2OH &\overset{K_3}{\rightleftharpoons} Fe(CN)_5(NONHOH)^{3-} + H_2O \qquad (3) \\ &\longrightarrow Fe(CN)_5(H_2O)^{3-} + N_2O \end{aligned}$$

$$\begin{aligned} &Fe(CN)_5(NONHOH)^{3-} \\ &\qquad \xrightarrow{NH_2OH} Fe(CN)_5(NH_2OH)^{3-} + N_2O + H_2O \qquad (4) \end{aligned}$$

No conclusions could be made on the fate of pentacyanohydroxylamineferrate(II) formed in reaction (4). Lunak and Veprek-Siska studied the kinetics between pH = 5–7 and found the following empirical rate equation for the initial rate:[18]

$$v_0 = (k_1 + k_2[OH^-])[Fe(CN)_5NO^{2-}][NH_2OH] \quad (5)$$

In contrast to eq (2) - (4), they suggested a pH independent parallel path (6) and (7):

$$Fe(CN)_5NO^{2-} + NH_2OH \overset{K_6}{\rightleftarrows} Fe(CN)_5(NONH_2OH)^{2-} \quad (6)$$

$$Fe(CN)_5(NONH_2OH)^{2-} \xrightarrow{k_7} Fe(CN)_5(H_2O)^{3-} + N_2O + H^+ \quad (7)$$

The effect of pH was interpreted by reactions (8) and (9):

$$Fe(CN)_5(NONH_2OH)^{2-} + OH^- \overset{K_8}{\rightleftarrows} Fe(CN)_5(NONHOH)^{3-} + H_2O \quad (8)$$

$$Fe(CN)_5(NONHOH)^{3-} \xrightarrow{k_9} Fe(CN)_5(H_2O)^{3-} + N_2O \quad (9)$$

Using labeled hydroxylamine containing ^{15}N and ^{18}O isotopes, Wolfe *et al.*, found that one of the nitrogen atoms and the oxygen atom of N_2O came from hydroxylamine.[19] They found formation of a small amount of ammonia and attributed this to the slow spontaneous disproportionation of hydroxylamine in alkaline medium. The first two steps of the mechanism suggested are the same as eq. (6) and eq. (8). The formation of a N_2O complex was proposed as the rate determining step:

$$Fe(CN)_5(NONHOH)^{3-} \xrightarrow{slow} Fe(CN)_5(N_2O)^{3-} + H_2O \quad (10)$$

In a second, slow step the N_2O complex decomposes yielding the aquo-complex:

$$Fe(CN)_5(N_2O)^{3-} + H_2O \xrightarrow{slow} Fe(CN)_5H_2O^{3-} + N_2O \quad (11)$$

The salt of $Fe(CN)_5(N_2O)^{3-}$ could not be prepared directly from pentacyanoammineferrate(II).

Later Mosquera *et al.*, had spectrophotometric results on the kinetics of the reaction.[20] They also found first and second order terms on hydroxylamine. The rate constant of the first order term was in a good agreement with that of Wolfe, *et al.*

Our preliminary experiments on the stoichiometry indicated that the reaction is more complicated than assumed earlier. It became obvious that in parallel with the reduction of coordinated nitrosyl, the catalytic decomposition of hydroxylamine also occurs. In this paper we present a kinetic investigation and a quantitative description of this rather complex reaction.

EXPERIMENTAL

"Analytical grade" chemicals were used without further purification. $Na_3Fe(CN)_5NH_3 \cdot 3H_2O$ was prepared from $Na_2Fe(CN)_5NO \cdot 2H_2O$ (Reanal) according to the literature.[21] The amounts of iron and sodium were analyzed by atomic absorption spectrometry.

The concentration of the hydroxylamine stock solution was occasionally checked by iodometric titration. The stoichiometry was investigated by measuring the volume of gases evolved using a traditional thermostated gas burette. The change in the concentration of the hydroxylamine during the reaction was also followed by titration. The reaction in this case was quenched by acidification with 10% sulphuric acid. The ammonia formed was determined by the usual way after distillation from the reaction mixture into sulphuric acid. The composition of the gaseous products was determined by an ATOMKI QGA 2 mass spectrometer.

The kinetic investigations were performed in an argon atmosphere. One to one molar ratio (0.08 M phosphate — borate) buffer was used in order to keep the pH constant during the reaction. The ionic strength was kept constant by 0.5 M Na_2SO_4 as an inert electrolyte.

The absorption spectra were recorded by Beckman Acta III, Specord M40 (Zeiss) and HP 8452 diode array spectrophotometers. The kinetic measurements were carried out with Hitachi 139 and Hitachi Model 2000 spectrophotometers with a homemade fast mixing unit using a 5 mm optical cell. The actual $[H^+]$was calculated from the measured pH after mixing the reactants.

RESULTS AND DISCUSSION

Stoichiometry

We found that significantly more N_2O formed than expected based on eq. (1), moreover large amounts of N_2 and NH_3 were found when hydroxylamine was in excess. In order to clarify the stoichiometry experiments were done using pentacyanoammineferrate(II) instead of the nitrosyl complex. (The aquopentacyanoiron(II) complex cannot be prepared, however, NH_3 forms a weak complex with pentacyanoferrate(II) residue. Therefore, after dissolution, practically complete aquation of the complex occurs.) The results of a comparative study are shown in Fig. 1a and 1b. The consumption of hydroxylamine, the change in pH and the volume of the gaseous products were measured for 15 min. The similarity of the curves representing the change in the amount of gas and the amount of decomposed hydroxylamine is remarkable but the initial decrease of pH in the case of the pentacyanonitrosylferrate(II) clearly shows a difference. The following considerations provide a basis for a quantitative explanation of the experimental findings. In both reactions a catalytic decomposition of hydroxylamine occurs. The possible stoichiometries are as follows:

$$4\,NH_2OH = N_2O + 2NH_3 + 2H_2O \qquad (12)$$

$$3NH_2OH = N_2 + NH_3 + 3H_2O \qquad (13)$$

In the case of pentacyanonitrosylferrate(II) the reduction of the coordinated nitrosyl also takes place according to eq. (1) leading a decrease in pH, and the consumption of one further mole hydroxylamine, as well as evolution of more gaseous product than in the reaction with pentacyanoammineferrate(II). Table 1 shows typical analytical results after 30 min reaction time. These results are satisfactorily explained by stoichiometric equations (1), (12) and (13). The calculation was made assuming all of the nitrosyl complex reacted, and the ratio of N_2 and N_2O reflects the contributions of reactions (12) and (13). As shown in Table 1, the experimentally determined and calculated data agree within 5%.

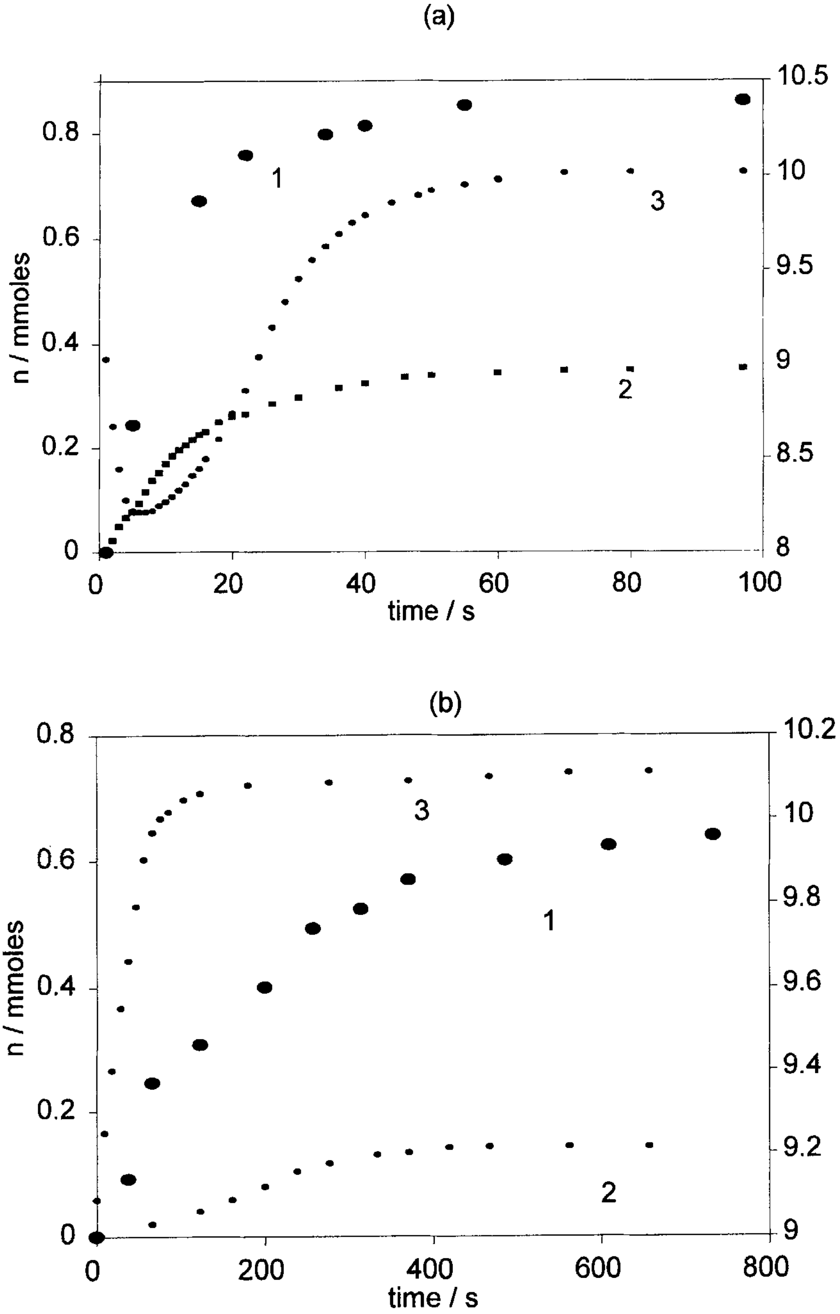


Figure 1 The amount of consumed hydroxylamine (1), evolved gases (2) and the change in pH (3) in the reaction of 0.01 M pentacyanonitrosylferrate(II) (a) or pentacyanoammineferrate(II) (b) with hydroxylamine (0.3 M). Volume of solutions: 11 cm^3.

Table 1 Measured and calculated analytical data in the reaction of $Fe(CN)_5NO^{2-}$ and NH_2OH

	Experimental results amount of components/(mole 10^{-3})				
time/min	$Fe(CN)_5NO^{2-}$	NH_2OH	N_2O	N_2	NH_3
0	0.52	6.32	0	0	0
30	0	1.06	1.16	0.64	1.85
change	0.52	5.26	1.16	0.64	1.85

	Calculated results after 30 min change in amount of components/(mole 10^{-3})				
No. of	$Fe(CN)_5NO^{2-}$	NH_2OH	N_2O	N_2	NH_3
reaction					
(1)	0.52	0.52	0.52	0	0
(13)	0	1.92	0	0.64	0.64
(12)	0.0	2.56	0.64	0	1.28
sum	0.52	5.0	1.16	0.64	1.92
Δ[a]	0[b]	0.26	0[c]	0[c]	0.07

[a] Δ means the difference between the experimental and calculated data. [b] The complete consumption of $Fe(CN)_5NO^{2-}$ was supposed in the calculation. [c] The difference is zero because the contribution of reactions (12) and (13) was determined from the experimental ratio of N_2O and N_2.

Kinetics of the reactions

Experiments were performed with hexacyanoferrate(II) to elucidate the role of coordination of hydroxylamine. This complex was found to be catalytically inactive. Addition of pyridine which forms a stable complex with $Fe(CN)_5^{3-}$, inhibited the decomposition of hydroxylamine. These findings indicate that coordination of hydroxylamine to $Fe(CN)_5^{3-}$ is a prerequisite for the catalytic effect of the complex.

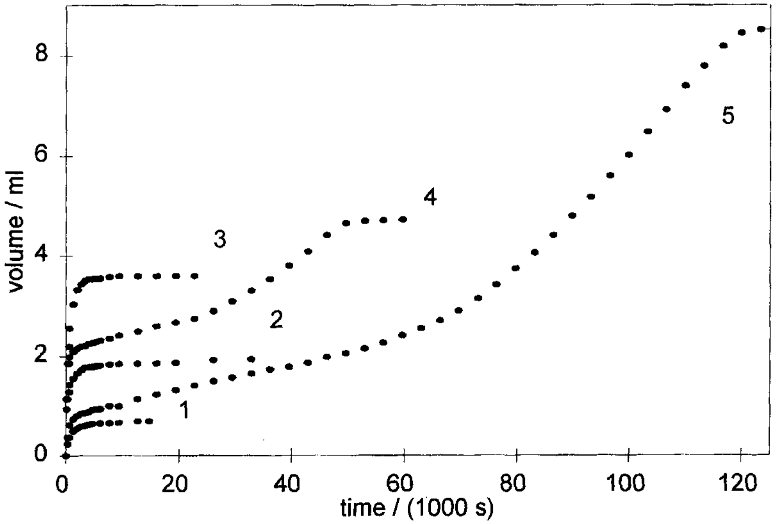


Figure 2 Volume of evolved gases as function of time at different hydroxylamine concentrations. $c_{Fe(CN)_5NO^{2-}} = 2 \times 10^{-3}$ M, $c_{NH_2OH} = 0.01$ M(1), 0.03 M(2), 0.05 M (3), 0.057 M (4), 0.1 M (5). Initial pH = 8.9.

The shapes of the curves obtained with the hydroxylamine — $Fe(CN)_5NH_3{}^{3-}$ system for volume of evolved gas *vs.* time depend on the ratio of the reactants and indicate rather complex kinetics (Fig. 2). When the excess of hydroxylamine is less than tenfold monotonous kinetic curves are obtained (curves 1–3 in Fig. 2), however three well defined parts of the curves can be distinguished with larger excesses (curves 4, 5 in Fig. 2). The inhibitory effect of high concentrations of hydroxylamine is indicated by these curves. The decrease of concentration of hydroxylamine in time results in reacceleration of the reaction towards the end of the process.

The spectrophotometric study of the same system gives a deeper insight into the mechanism of the reaction. Because of the molar absorbances of the species, the concentration ranges in the spectrophotometric and the gas volumetric experiments are rather different. The absorbance *vs.* time curves at 445 nm are shown in Fig. 3. Curves 1–3 in Fig. 3 are due to formation of an intermediate and the broadening of the maxima with increasing excess of hydroxylamine is a clear indication of the formation of a less active catalytic complex.

Quantitative comparison of gas volumetric and spectrophotometric results is difficult because of the large difference in concentrations. However, the shapes of the curves suggest a self-inhibition type reaction.[22] At low concentration of hydroxylamine the originally formed complex

$$Fe(CN)_5H_2O^{3-} + NH_2OH \overset{K_{14}}{\rightleftarrows} Fe(CN)_5(NH_2OH)^{3-} + H_2O \qquad (14)$$

reacts with another pentacyanoaquoferrate(II) and a binuclear complex is formed:

$$Fe(CN)_5(NH_2OH)^{3-} + Fe(CN)_5H_2O^{3-} \overset{K_{15}}{\rightleftarrows} (CN)_5FeNH_2OHFe(CN)_5^{6-} + H_2O \qquad (15)$$

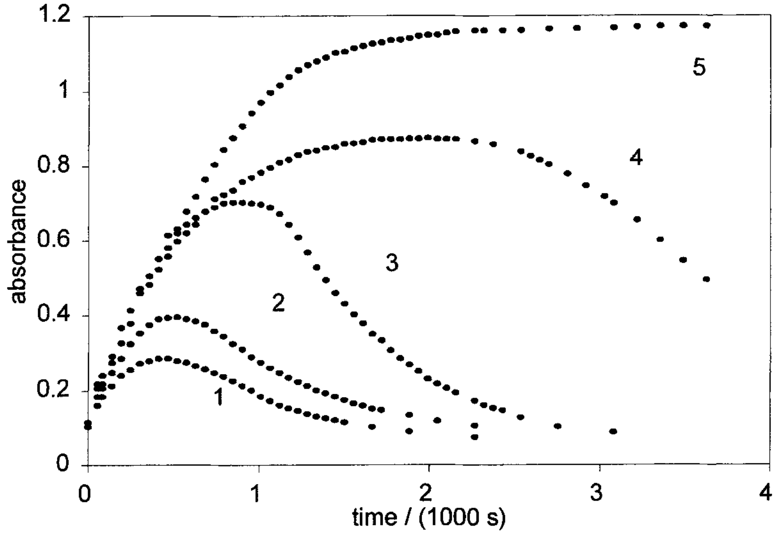


Figure 3 The change of absorbance at 445 nm as a function of time at different hydroxylamine concentration $c_{Fe(CN)_5NH_3^{3-}} = 5 \times 10^{-4}$ M, $c_{NH_2OH} = 5 \times 10^{-3}$ M(1), 6×10^{-3} M(2), 7×10^{-3} M(3), 7.2×10^{-3} M (4), 8×10^{-3} M(5). Initial pH = 9.0. Curve (5) falls to the final absorbance after 10 hours.

The homolytic decomposition of the bridging hydroxylamine results in HO· and NH_2· radicals and their reactions lead to the formation of N_2, N_2O and NH_3. Excess hydroxylamine favors formation of a catalytically inactive or less active mononuclear complex. According to this interpretation the absorption maximum at 445 is assigned to the pentacyanohydroxylamineferrate(II) complex, in agreement with an earlier publication.[6] However, formation of mononuclear complexes $Fe(CN)_5X^{3-}$ is fast[21] with a half time certainly less than 0.1 s, while our kinetic experiments indicate that the formation of an intermediate takes place in several hundred seconds. Therefore, it is suggested that the intermediate is another nitrosylcomplex formed in the following reaction:

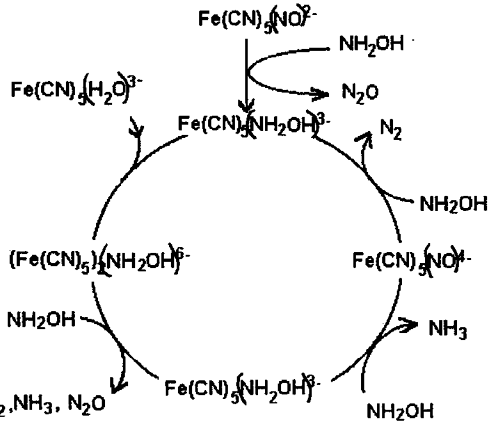
$$Fe(CN)_5(NH_2OH)^{3-} + NH_2OH \rightarrow Fe(CN)_5NO^{4-} + NH_4^+ + H_2O \qquad (16)$$

This type complex has already been assumed as an intermediate in the decomposition of hydroxylamine catalyzed by $Ni(CN)_4^{2-}$.[23,24] Substitution of one cyanide ion by hydroxylamine was assumed as the first step. We believe that such a substitution reaction is very unlikely because of the additional high stability of the tetracyanonickel(II) complex. However, it is well known[25] that one additional ligand may be taken up by $Ni(CN)_4^{2-}$, so the coordination of hydroxylamine to $Ni(CN)_4^{2-}$ may occur and the pentacoordinated species can react with one further molecule of hydroxylamine to give the nitrosyl complex.

Reaction with a third hydroxylamine results in formation of dinitrogen:

$$Fe(CN)_5(NO)^{4-} + NH_2OH \rightarrow Fe(CN)_5(H_2O)^{3-} + N_2 + OH^- \qquad (17)$$

Reactions (16) and (17) correspond stoichiometrically to eq. (13). These steps result in slow disproportionation of hydroxylamine, yielding N_2 in the "plateau" range of the absorbance *vs.* time curves (Fig. 3), until the concentration of hydroxylamine decreases permitting formation of the binuclear complex responsible for fast decomposition. Scheme 1 summarizes the mechanism:



Scheme 1

We have indirect experimental evidence supporting this scheme. If the reaction is initiated in the presence of acrylonitrile a white precipitate formed indicating polymerization initiated by radicals. Furthermore, it is known that pentacyanonitrosylferrate(II) gives a color reaction with HS^- (Gmelin reaction).[26] We studied spectrophotometrically the pentacyanoammineferrate(II) — hydroxylamine — HS^- system. The absorption spectra of Fig. 4a show a red intermediate formed with an absorption maximum at 560 nm. Fig. 4b shows that in the reaction between pentacyanonitrosylferrate(II) and HS^- an intermediate appears with a similar absorption maximum. Although these spectra are not regarded as direct proof of the formation of $Fe(CN)_5NO^{4-}$, they support the formation of a reduced form of the nitrosyl complex.

Since Scheme 1 is too complicated for quantitative numerical analysis, a minimum model was constructed. For the decomposition of hydroxylamine catalyzed by pentacyanoaquoferrate(II) the following three reactions were considered as crucial steps:

$$A + B \xrightarrow{k_1} C \tag{18}$$

$$C \xrightarrow{k_{-1}} A + B \tag{19}$$

$$C + A \xrightarrow{k_2} 2A + P \tag{20}$$

where A stands for pentacyanoammineferrate(II), B stands for hydroxylamine, C symbolizes the intermediate which is responsible for light absorption at 445 nm and P is the gaseous product. This minimum model describes the characteristics of the experimental curves surprisingly well (cf. Fig. 2. 3, and 5).

The kinetics of the reaction between pentacyanonitrosylferrate(II) and hydroxylamine was followed spectrophotometrically at 445 nm. As the Fig. 6 shows, the absorbance first increases, then decreases, but the shape of the curves indicates more complex kinetics than a simple consecutive scheme. The curves are highly sensitive to pH and the initial concentrations. In order to quantitatively analyze, we first tried to ensure *pseudo* zero order conditions with application of a large excess of hydroxylamine and buffer. However, the buffer capacity of the solution was not enough to keep the pH constant for the whole reaction. In order to describe the reaction the model represented by eq. (18–20) was completed with the following two reaction paths:

$$D + B \xrightarrow{k'_{r1}} A + P \tag{21}$$

$$D + 2B \xrightarrow{k'_{r2}} C + P \tag{22}$$

where D stands for $Fe(CN)_5NO^{2-}$. In order to obtain the rate constants a few curves at different pH's and concentrations were considered and the k_i rate constants in eq. (18–22) were varied to obtain the best fit. The calculations were carried out by a semi-implicit Runge-Kutta algorithm. The quality of the fits were assessed by visual comparison of the experimental and calculated curves. From the calculation we came to the conclusion that k'_{r1} and k'_{r2} are *pseudo* second and third order rate constants, *i.e.* both showed a linear dependence on $[OH^-]$. Therefore, reduction of the coordinated nitrosyl can be represented by the following rate equation:

$$\frac{d[Fe(CN)_5NO^{2-}]}{dt} = (k_{r1} + k_{r2}[NH_2OH])[NH_2OH][Fe(CN)_5NO^{2-}][OH^-] \quad (23)$$

With the given k_{r1} and k_{r2} rate constants we checked whether all measured curves could be described. No further refinement was made because of the large number

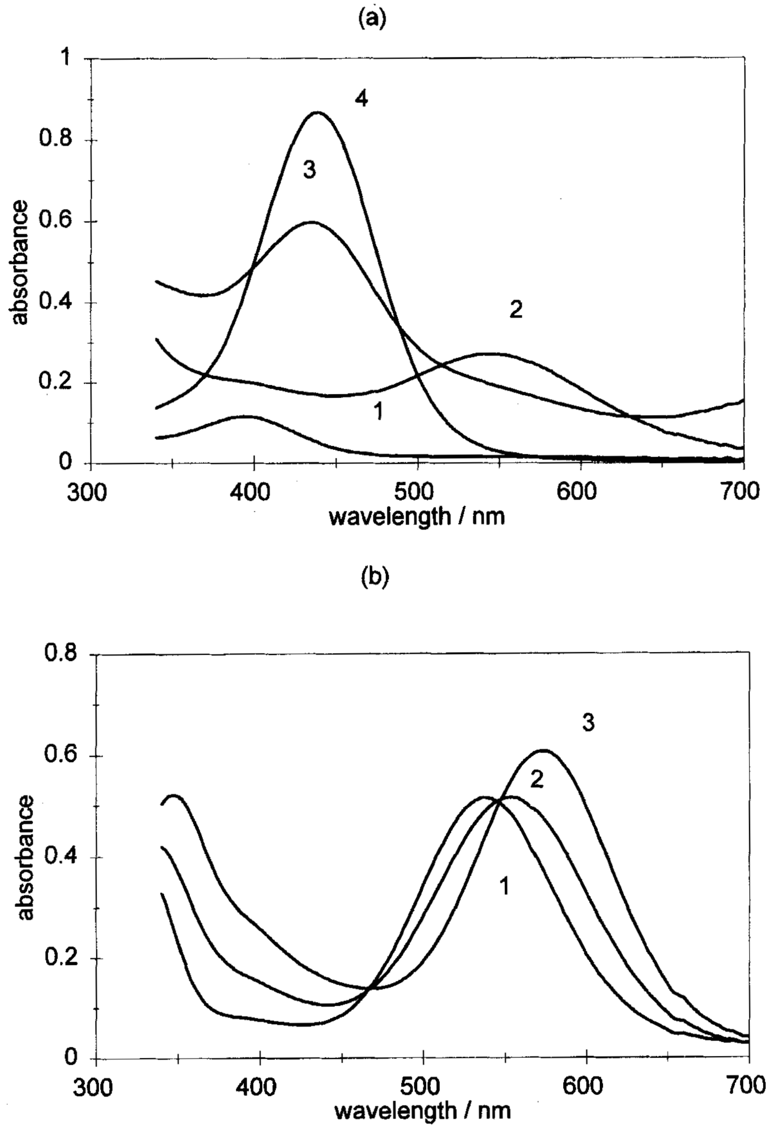


Figure 4 Change of absorption spectra as a function of time. (a) 4×10^{-4} M $Fe(CN)_5NH_3^{3-}$, 4×10^{-3} M NH_2OH, 10^{-3} M HS^- solution; (1) 1 s, (2) 200 s, (3) 400 s and (4) without sulphide after 400 s. (b) 4×10^{-4} M $Fe(CN)_5NO^{2-}$ and 10^{-3} M HS^- solution; (1) 1s, (2) 5 s, (3) 50 s. pH = 9.0.

of experimental curves. The results are shown in Fig. 6. It can be seen that the calculated curves fit well to the experimental ones. Representative examples were chosen from the concentration and pH range. Sometimes larger deviations were found (curve 5 in Fig. 6.) probably because of gas evolution in the cell. Since our study focused on reduction of coordinated nitrosyl we do not deal in detail with the rate

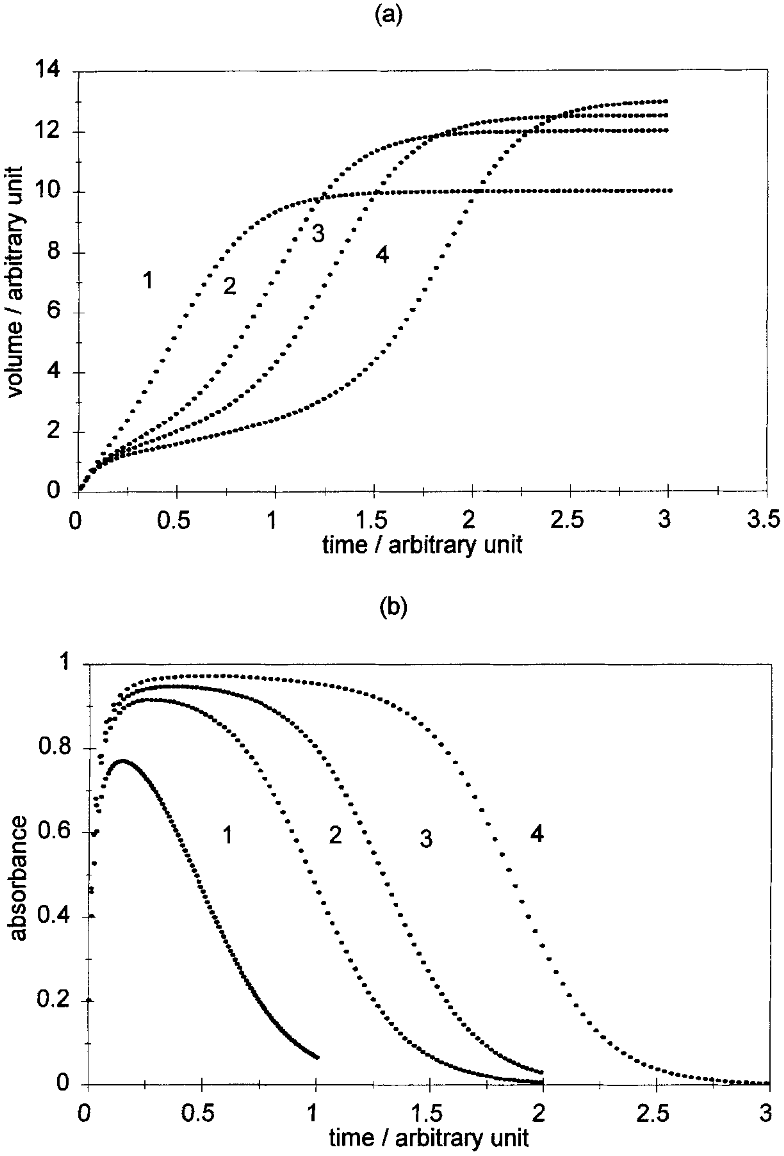


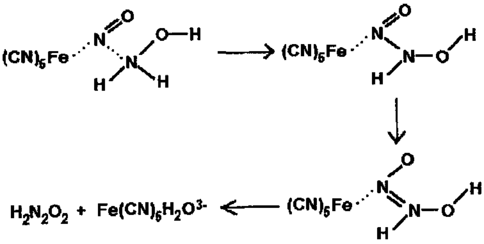
Figure 5 Calculated change of gas volume (a) and absorbance (b) *vs.* time curves based on the model represented eq. (18)–(20). $k_1 = 5$, $k_{-1} = 0.1$, $k_5 = 5.0$. $A_0 = 1$, $B_0 = 10(1), 12(2), 12.5(3), 13(4)$.

equation for disproportionation. Table 2 shows the rate constants according to the model. It is important to note that, in order to obtain good fit, we had to vary k_2 in all curves. The variation of k_2 with concentration could not be expressed with an empirical rate equation. The probable reason is that a complicated series of reactions is involved in the reaction represented by k_2, radical chain reactions, as discussed later. The comparable rate constant, k_1, differs from the previously determined ones[18,19] (Table 2). This deviation is attributed to the different model and the presence of a second order term on hydroxylamine in our rate equation (23) which is not included in earlier studies (5).[18,19]

The form of rate equation (23) agrees well with the earlier published ones[17–19] even though catalytic disproportionation was not recognized in these papers. The possible explanation is that in all previous studies the initial rate method was used to determine the rate equation. Also this fact supports that extrapolating the mechanism to zero time, only reduction of nitrosyl takes place. However, from the moment that pentacyanoaquoferrate(II) appears disproportionation of hydroxylamine becomes dominant.

Interpretation of Scheme 1

The first step is probably the preequilibrium written by eq. (6). Then the coordination stabilizes a form in which the N of the nitrosyl probably has a lower oxidation state than (+3) while the N of hydroxylamine is higher than −1:



Scheme 2

We propose that the oxidation states of both nitrogens are the same (+1). The next step is substitution, with contribution of a water molecule or another hydroxylamine, in which the hyponitrite-like ligand leaves the coordination sphere. But at this pH the hyponitrous acid like intermediate deprotonates and decomposes:[27]

$$H_2N_2O_2 \rightarrow N_2O + H_2O \qquad (24)$$

The half time of this decomposition is ca. 15 min at 25°C at pH = 9.2[28] which is similar to that measured gas-volumetrically. However, at different concentrations we obtained a shorter half time for gas evolution indicating that the intermediate is probably not hyponitrous acid, but its active form.

The existence of a second-order term for hydroxylamine indicates that the rate-determining step is probably substitution. Ligand substitution of pentacyanoferrate(II) complexes is rapid,[21] however the pentacyanonitrosylferrate(II) has some iron (III) character because of the strong back-bonding[4] therefore slower ligand

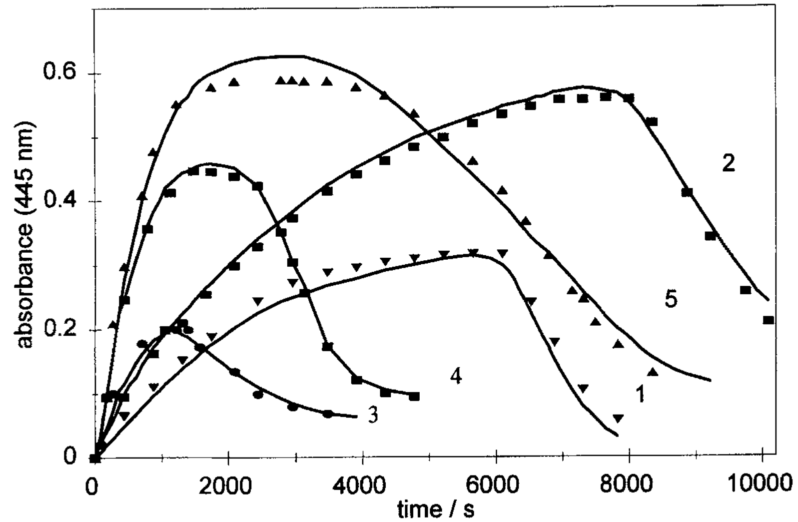


Figure 6 Measured (symbols) and calculated (solid) absorbance *vs.* time curves in the reaction between $Fe(CN)_5NO^{2-}$ and $NH_2OH \cdot c_{Fe(CN)_5NO^{2-}} = 2 \times 10^{-4}$ M, $c_{NH_2OH} = 1 \times 10^{-3}$ M(1), 2×10^{-3} M(2), 3×10^{-3} M(3) at pH 9.2 and 2×10^{-3} M(4), 3×10^{-3} M(5) at pH 8.2.

exchange may be expected for the complexes formed after addition of the substrate. In the case of primary amines we have direct evidence for this substitution controlled electron transfer.[15] One interpretation of the mechanism is very close to that of Wolfe, *et al.*[19] except that we suggest formation of N_2O out of the coordination sphere. Our mechanism is supported by the fact that the $Fe(CN)_5(N_2O)^{3-}$ complex could not be prepared.

Catalytic disproportionation of hydroxylamine takes place *via* two parallel paths. The first, for which the contribution of a binuclear complex is suggested, probably occurs through formation of radicals:

$$\begin{gathered}
(CN)_5FeNH_2OHFe(CN)_5^{6-} \rightarrow 2\ Fe(CN)_5^{3-} + NH_2\cdot + \cdot OH \\
NH_2\cdot + NH_2OH \rightarrow NH_3 + \cdot NHOH \\
HO\cdot + NH_2OH \rightarrow H_2O + \cdot NHOH \\
\cdot NHOH + NH_2OH \rightarrow NH_3 + HNO + \cdot OH \\
2HNO \rightarrow N_2O + H_2O \\
2\cdot NHOH \rightarrow N_2 + H_2O
\end{gathered} \tag{25}$$

Table 2 The estimated kinetic parameter for the reactions.

rate constant	this paper	ref 18	ref 19
k_{r1}	6×10^4 M^2 s^{-1}	3.8×10^5 M^2 s^{-1}	3.1×10^6 M^{-2} s^{-1}
k_{r2}	2×10^6 M^{-3} s^{-1}	no data	no data
k_1	33 M^{-1} s^{-1}	no data	no data
k^{-1}	9×10^{-3} s^{-1}	no data	no data
k_2	could not be determined[a]		

[a] see text

In the reduction oxidation reactions of hydroxylamine radicals appear quite often.[29,30]

The second path is slower and the intermediate is probably $Fe(CN)_5NO^{4-}$. Decomposition of this complex may occur by reduction of NH_2OH as eq. (17) shows. A further possibility is substitution by water or another hydroxylamine:

$$Fe(CN)_5NO^{4-} \xrightarrow{H_2O} Fe(CN)_5(H_2O)^{3-} + NO^- \quad (26)$$

$$Fe(CN)_5NO^{4-} \xrightarrow{NH_2OH} Fe(CN)_5(NH_2OH)^{3-} + NO^- \quad (27)$$

$$2NO^- + 2H^+ \longrightarrow N_2O + H_2O \quad (28)$$

the leaving NO^- ion protonates and decomposes to N_2O as written in eq. (28).

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