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The Reaction of Pentacyanonitrosylferrate(II) with Bases. V. Thiocyanate

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Received September 7, 1970

Observations are reported which suggest that the blue species, species B (λ_{max} = *580 to 590 nm), which forms when pentacyanonitrosylferrate(II) (nitroprusside,* $(NC)_5FeNO^{2-}$*)—thiocyanate mixtures are irradiated or made basic and then acidic, results from the reaction of thiocyanate with* $(NC)_5FeNO_2^{4-}$ *and* $(NC)_5FeH_2O^{3-}$:

$$(NC)_5FeNO_2^{4-} + NCS^- = (NC)_5FeNCS^{4-} + NO_2^- \qquad (3)$$

$$(NC)_5FeH_2O^{3-} + NCS^- = (NC)_5FeNCS^{4-} + H_2O \qquad (4),$$

followed by the oxidation of $(NC)_5Fe^{II}NCS^{4}$ *by nitrous acid to yield* $(NC)_5Fe^{III}NCS^{3-}$*, species* B.

Introduction

When a mixture of pentacyanonitrosylferrate(II) (nitroprusside, $(NC)_5FeNO^{2-}$) and thiocyanate in aqueous solution is irradiated, a blue color develops,[2] species *B* (λ_{max} between 580 and 590 nm).[3] A similar spectrum is observed when a $(NC)_5FeNO^{2-}$—thiocyanate mixture is made basic and then acidic.[3] It has been proposed in both cases that the observed species results from an interaction between thiocyanate and $(NC)_5FeNO_2H^{3-}$ to form an addition product $(NC)_5FeNO_2H(NCS)^{4-}$. This note reports supplemental observations on the $(NC)_5FeNO^{2-}$—thiocyanate system which suggest an alternate reaction scheme to account for the formation of *B*.

Experimental Section

Chemical and Solutions. All chemicals were of reagent grade purity. Solutions were prepared by weighing the desired chemicals into doubly distilled water. Analyses were carried out using standard techniques. The solutions containing $(NC)_5FeNO^{2-}$ and other species capable of undergoing photochemical reactions were protected from the light. Solutions used in experiments carried out in the absence of oxygen were flushed with nitrogen (99.99 percent) for at least ten minutes. The sodium acetate-acetic acid buffers were prepared so that the total [Na^+] was 1.0 *M* (NaO_2CCH_3 and NaCl) and the sum of the acetate ion and acetic acid concentrations was 1.0 *M*. In the tables initial and final concentrations are listed. Initial and final concentrations refer to the concentrations of the species present before and after the dilution rescribed in the experiment was performed.

Instruments. Spectral measurements were made with a Perkin-Elmer 202 Spectrophotometer and a thermostated Bausch and Lomb Spectronic 505 using one centimeter cells. The hydrogen ion activities were measured with a Radiometer pH Meter 28 using a combination calomel- glass electrode standardized with commercial buffers.

Results and Discussion

The primary equilibria present in solution when $(NC)_5FeNO^{2-}$ is made basic are:

$$(NC)_5FeNO^{2-} + 2OH^- = (NC)_5FeNO_2^{4-} + H_2O \qquad (1)$$

and

$$(NC)_5FeNO_2^{4-} + H_2O = (NC)_5FeH_2O^{3-} + NO_2^- \qquad (2).$$

The equilibrium concentration quotient for (1) has been determined in aqueous solutions containing a variety of electrolytes.[4,5,6,7] The value depends both on the nature and the concentration of the added electrolyte. From kinetic[6,7] and polarographic measurements[7,8] (1) is found to consist of two steps:

$$(NC)_5FeNO^{2-} + OH^- = (NC)_5FeNO_2H^{3-} \qquad (1')$$

$$(NC)_5FeNO^2H^{3-} + OH^- = (NC)_5FeNO_2^{4-} + H_2O \qquad (1'').$$

The equilibrium concentration quotient and rate constants for (2) have been determined.[6,9]

Observations are noted here which suggest that the process by which *B* is formed is the substitution in basic solution of nitrite and water in $(NC)_5FeNO_2^{4-}$ and/or $(NC)_5FeH_2O^{3-}$ (formed in (1) and (2)) by thio-

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[2] N. Tarugi, *Ann. Chem. Applic.*, *16*, 407 (1926); *ibid*, *17*, 519 (1927); *Chem. Abstr.*, *21*, 865 (1927).

[3] J. Dempir and J Mašek, *Inorg. Chim. Acta*, *2*, 402 (1968).

[4] I. M. Kolthoff and P. E. Toren, *J. Amer. Chem. Soc.*, *75*, 1197 (1953).

[5] P. Zuman and M. Kabát, *Chem. Listy*, *48*, 358 (1954).

[6] J. H. Swinehart and P. A. Rock, *Inorg. Chem.*, *5*, 573 (1966).

[7] J. Mašek and H. Wendt, *Inorg. Chim. Acta*, *3*, 455 (1969)

[8] J. Mašek and J. Dempir, *Inorg. Chim. Acta*, *2*, 443 (1968).

[9] J. H. Swinehart, *Coord. Chem. Revs.*, *2*, 385 (1967)

cyanate:

$$(NC)_5FeNO_2^{4-}+NCS^- = (NC)_5FeNCS^{4-}+NO_2^{-\ 10} \qquad (3)$$

$$(NC)_5FeH_2O^{3-}+NCS^- = (NC)_5FeNCS^{4-}+H_2O \qquad (4),$$

followed by the oxidation of $(NC)_5Fe^{II}NCS^{4-}$ by nitrous acid, HNO_2, or $H_2NO_2^+$ to yield $(NC)_5Fe^{III}NCS^{3-}$, species *B*.

If the proposed mechanism is correct: (i) an interaction between thiocyanate, and $(NC)_5FeNO_2^{4-}$ and $(NC)_5FeH_2O^{3-}$ should occur; (ii) the degree of formation of *B* should parallel the degree of interaction of thiocyanate with $(NC)_5FeNO_2^{4-}$ and $(NC)_5FeH_2O^{3-}$; and (iii) the rate of formation of *B* should be dependent on the concentration of the oxidizing agent, HNO_2 or $H_2NO_2^+$. The following experiments test these predictions.

Table I. Effect of Tiocyanate on Equilibrium A_{395nm}[a]

Expt.	$10^4[(NC)_5FeNO^{2-}]_{initial}$ *M*	$[OH^-]$ *M*	$[NCS^-]$ *M*	$[Cl^-]$ *M*	A_{395nm}
1	2.5	0.50	—	0.50	0.40
2	2.5	0.50	—	0.50(ClO_4^-)[b]	0.40
3	2.5	0.50	0.50	—	0.13
4	4.0	0.25	—	0.75	0.86
5	4.0	0.25	0.12_5	0.62_5	0.57
6	4.0	0.25	0.25	0.50	0.50
7	4.0	0.25	0.25[c]	0.50	0.50
8	4.0	0.25	0.75	—	0.35

[a] Temperature 25°C, $\mu=1.0(Na^+)$. [b] $NaClO_4$ used in place of NaCl. [c] Added as solid NaSCN 1.5 minutes after $(NC)_5FeNO^{2-}$—OH^- reaction initiated.

Table II. Dependence of A_{395nm} on Nitrite and Thiocyanate Concentrations[a]

Expt.	$10^4[NC)_5FeNO^{2-}]_{initial}$ *M*	$10^3[NO_2^-]$[b] *M*	$[NCS^-]$ *M*	$[OH^-]$ *M*	A_{585nm}
1	10.0	—	0.50	0.10	2.0_2
2	10.0	2.0	0.50	0.10	1.6_7
3	10.0	—	0.20	0.10	1.7_8
4	10.0	2.0	0.20	0.10	0.7_6
5	4.0	10.1	0.15	0.05	0.0_9
6	4.0	5.5	0.15	0.05	0.1_4
7	4.0	2.6	0.15	0.05	0.2_1
8	4.0	1.1	0.15	0.05	0.2_8

[a] Temperature 25°C, $\mu=1.0(Na^+)$. [b] Nitrite is produced from (2). The concentration of nitrite indicated is that added $NaNO_2$.

1. Table I summarizes the effect of thiocyanate on the equilibrium absorbance at 395 nm, A_{395nm}. At this wavelength the extinction coefficients of $(NC)_5FeNO_2^{4-}$ and $(NC)_5FeH_2O^{3-}$ are $3.1\times10^3\ M^{-1}\ cm^{-1}$[6] and $1.1\times10^3\ M^{-1}\ cm^{-1}$[11] respectively. The equilibrium concentration quotient for (2), as reflected by A_{395nm}, is independent of whether the anion is chloride or perchlorate at $[Na^+]=1.0\ M$ (expts. 1 and 2). However, the addition of thiocyanate at constant $[Na^+]$ decreases A_{395nm}, suggesting a decrease in the concentrations of $(NC)_5FeNO_2^{4-}$ and $(NC)_5FeH_2O^{3-}$. The experiments were carried out be adding hydroxide-thiocyanate solutions to $(NC)_5FeNO^{2-}$ solutions or hydroxide solutions to $(NC)_5FeNO^{2-}$—thiocyanate solutions. In expt. 7 solid NaNCS was added 1.5 minutes after the $(NC)_5FeNO^{2-}$—hydroxide reaction (1) had been initiated. This experiment eliminates the possibility that the decrease in A_{395nm} with increasing thiocyanate results from a reaction between thiocyanate and $(NC)_5FeNO_2H^{3-}$, the latter being formed in (1′). Under the experimental conditions the half-life of the $(NC)_5FeNO^{2-}$—hydroxide reaction (1) is about five seconds,[6] and if the thiocyanate- $(NC)_5FeNO_2H^{3-}$ reaction was operative, A_{395nm} would be larger in expt. 7 than in expt. 6.

2. Table II shows the eeffct of added nitrite and thiocyanate on the absorbance at 585nm, A_{585nm} (species *B*). Solutions of the initial concentrations indicated in Table II were prepared and allowed to equilibrate for 30 minutes at 25°C. In expt. 1-4 the values of A_{585nm} were those obtained after the addition of a constant volume of dilute HCl (approximately 2.7 ml) to 50 ml of solution in order to bring the pH to 4.0±0.1. In expt. 5-8 an equal volume of buffer (pH=5.0) was added to the solution and A_{585nm} was measured. These experiments indicate that $(NC)_5FeNO_2^{4-}$ is not a precursor to *B*, as represented by A_{585nm}. If $(NC)_5FeNO_2^{4-}$ is a precursor, A_{585nm} should be larger in those experiments having larger $[NO_2^-]$ due to the effect of nitrite on (2), (3), and (4).

3. When a solution of the following composition: $[(NC)_5FeNO^{2-}]=8.0\times10^{-4}\ M$, $[Na^+]=[Cl^-]$ 1.00 *M*; is mixed with solutions of the following compositions:

(i) $[OH^-]=0.10M$, $[SCN^-]=0.30M$, and $[Cl^-]=0.60M$

(ii) $[OH^-]=0.20M$, $[SCN^-]=0.30M$, and $[Cl^-]=0.50M$,

(10) The notation $(NC)_5FeNCS^{4-}$ does not mean that thiocyanate is necessarily N-bonded to iron.
(11) S. Iimori, *Z. Anorg. Allgem. Chem.*, *167*, 145 (1927).

a reaction between the $(NC)_5FeNO_2^{4-}$ initially produced (1), and thiocyanate is observed. The experiments were carried out under conditions where (2) did not directly interfer. The observed reaction was insensitive to light and the presence of oxygen. At various times aliquots of the above solution were mixed with an equal volume of $pH=5$ buffer (see Experimental Section). Figure 1 shows a plot of the absorbance at 585nm, A_{585nm}, and the absorbance at 395nm at any time minus the final absorbance at that wavelength, ΔA_{395nm}, versus time. The initial increase observed for the 395nm data at times less than one minute corresponds to (1).[6,7] The increase in A_{585nm} follows the decrease in ΔA_{395nm}. This suggests that the degree of formation of *B* versus time parallels the degree of interaction of thiocyanate with $(NC)_5FeNO_2^{4-}$ and $(NC)_5FeH_2O^{3-}$ versus time.

Table III. Effect of Nitrite and Hydrogen Ion Concentrations on the Kinetics of Formation of *B* [a].

$10^3[NO_2]_{final}$ *M*	$10^6[H^+]_{final}$ *M*	$t_{1/2}$ [b] sec.	$[SCN^-]_{initial}$ M
9.2_7	3.1_6	$25._1$	0.15
4.9_3	"	$47._2$	"
2.4_6	"	$84._0$	"
1.0_8	"	$157._3$	"
9.9_0	"	$47._1$	0.30
4.2_4	"	$87._9$	"
2.2_8	"	$175._3$	"
6.5_9	$12._6$	$9._5$	"
2.4_6	"	$23._4$	"
10.0_0	"	$6._0$	0.15
5.0_0	"	$12._5$	"
2.5_0	"	$23._4$	"
1.0_0	"	$56._6$	"
2.7_5	"	$19._5$	"
2.7_8	"	$18._5$	"

[a] In all cases λ_{max} was between 580 and 590_{nm}. Temperature 26°C, $\mu=1.0(Na^+)$. $[(NC)_5FeNO^{2-}]_{initial}=4.0x10^{-4}M$ except in the last experiment where it was $2.0x10^{-4}M$. [b] Half-life of pseudo-first order plot.

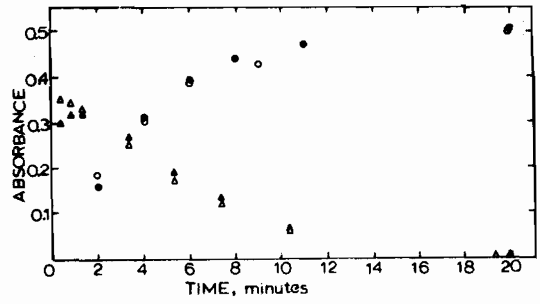

Figure 1. Plot of A_{585nm} (circles) and ΔA_{395nm} (triangles) versus time for solutions having the final concentrations: $[(NC)_5FeNO^{2-}]=4.0x10^{-4}M$, $[OH^-]=0.10M$, $[SCN^-]=0.15M$, $[Cl^-]=0.75M$, $[Na^+]=1.00M$ ○ and △), and $[(NC)_5FeNO^{2-}]=4.0x10^{-4}M$, $[OH^-]=0.05M$, $[SCN^-]=0.15M$, $[Cl^-]=0.80M$, $[Na^+]=1.00M$ ● and ▲). Temperature 24°C.

4. Table III presents data dealing with the rate of formation of *B*, as reflected by A_{585nm}, as a function of the hydrogen and nitrite ion concentrations. The experiments were performed by mixing a $(NC)_5FeNO^{2-}-OH^--SCN^-$ containing solution with an equal volume of buffer which contained added nitrite. The $(NC)_5FeNO^{2-}-OH^--SCN^-$ solutions were allowed to equilibrate for at least 20 minutes, which was a sufficient time for the system to reach equilibrium (see Figure 1). Pseudo-first order plots were made of the absorbance data at 585nm. In all cases the total nitrite concentration was in excess over the initial concentration of $(NC)_5FeNO^{2-}$. Figure 2 is a plot of k_{obs} $(=\frac{0.693}{t_{1/2}})$ versus $[HNO_2]$. The $[HNO_2]$ was calculated from $[NO_2^-]_{final}$ and $[H^+]_{final}$ using $[H^+][NO_2^-]/[HNO_2]=4.5\times10^{4-}$.[12] The value of the second-order rate constant, $0.693/t_{1/2}[HNO_2]$, is 425 M^{-1} sec^{-1} at 26°C and $\mu=1.0$ (Na^+). This observation indicates that *B* is formed in a reaction between nitrous acid and the iron-containing complex precursor to *B*. At lower pHs it is possible that $H_2NO_2^+$ also acts as an oxidizing agent. It should be noted that a second, unknown reaction is operative. If the nitrite or hydrogen ion concentrations are too large, a species forms having an absorbance maximum at approximately 550nm (or between 550 and 590nm depending on the amounts of the two products formed). In all experiments reported here the absorbance maximum was between 580 and 590nm. The second reaction is under investigation.

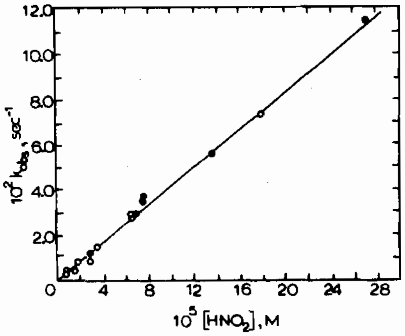

Figure 2. Plot of $k_{obs}(sec^{-1})$ versus $[HNO_2]$ (*M*) for the reaction between te precursor of *B* ad excess itrous acid. Temperature 26°C ad $\mu=1.0(Na^+)$.

In summary, observations 1 and 2 indicate an interaction between $(NC)_5FeNO_2^{4-}$ and $(NC)_5FeH_2O^{3-}$, and thiocyanate. The degree of this interaction, as expressed by the kinetic and equilibrium measurements, parallels the degree of formation of *B* (observations 2 and 3). Observation 4 indicates that the rate of formation of *B* is proportional to the concentration of nitrous acid, and observations 1 and 2 suggest that $(NC)_5FeNO_2^{4-}$, and hence $(NC)_5FeNO_2H^{3-}$, are not precursors to *B*. Additionally, the spectrum of $(NC)_5Fe^{III}NCS^{3-}$ has been reported[13] and agrees well with the spectrum of B^3.

The reactions between $(NC)_5Fe^{II}NH_3^{3-}$, and azide or thiocyanate in the presence of oxidizing agents such as oxygen, hydrogen peroxide and $Fe(CN)_6^{3-}$ have been studied.[13,14] The results of these studies suggest that

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(12) « Stability Constants of Metal-Ion Complexes », L. G. Sillen and A. E. Martell Eds., The Chemical Society, London, 1964, p. 164

(13) B. Jaselskis, *J. Amer. Chem. Soc.*, *83*, 1082 (1961).

(14) B. Jaselskis and J. C. Edwards, *Anal. Chem.*, *32*, 381 (1960).

azide or thiocyanate displaces ammonia in $(NC)_5FeNH_3^{3-}$ and that the oxidizing agents oxidize the resulting complexes to $(NC)_5Fe^{III}N_3^{3-}$ or $(NC)_5Fe^{III}NCS^{3-}$.

The photochemical reaction of $(NC)_5FeNO^{2-}$ in the presence of thiocyanate which results in the production of *B* is of interest. It has been reported that the irradiation of $(NC)_5FeNO^{2-}$ yields $(NC)_5Fe^{II}H_2O^{3-}$ [15] and that the solutions become acidic,[16] presumably from the reaction

$$NO^+ + 2OH^- = NO_2^- + H_2O.$$

It seems reasonable that the thiocyanate reacts with $(NC)_5Fe^{II}H_2O^{3-}$ by (4) producing $(NC)_5Fe^{II}NCS^{4-}$, which is then oxidized by nitrous acid to $(NC)_5Fe^{III}NCS^{3-}$. To test this proposal thiocyanate was added to irradiated solutions of $(NC)_5FeNO^{2-}$, and A_{585nm} and A_{395nm} were followed. As A_{395nm} decreased, A_{585nm} increased. First order plots at both wavelengths were linear, and the slope was proportional, at constant ionic strength, to the concentration of excess thiocyanate. At 25°C and $\mu = 0.2$ (NaCl and NaSCN) the bimolecular rate constant was $0.14 \pm 0.10\, M^{-1}\ sec^{-1}$. The final pH of the solution after irradiation was 3.5. This experiment suggests that the proposed mechanism is operative.

Acknowledgments. This work was carried out at the Department of Chemistry, Faculty of Mathematical and Physical Sciences, and Faculty of Science, University of Chile, Santiago, Chile and the Institute for Inorganic Chemistry, University of Basel, Switzerland. One of the authors (J.H.S.) acknowledges support from the Organization of American States Multinational Program, the John Simon Guggenheim Foundation, and Professor S. Fallab of the University of Basel. Both authors acknowledge support from « Cenvenio: University of Chile - University of California ». Helpful discussion with Dr. Ruben Levitus and Mr. Steven Wolfe are acknowledged.

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(15) D. Baudisch, *Science*, *108*, 443 (1948).

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