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# Reaction of the Nitroprusside Ion with Thiocyanate and Some Other Ligands

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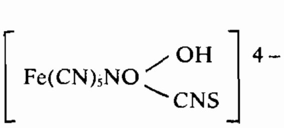
*It was found that the known photochemically induced colour reactions between the nitroprusside ion and thiocyanate, or some other ligands, proceed also without irradiation when the alkaline reaction mixture is acidified. From the study of these reactions which were observed with thiocyanate, azide, thiosulfate, and thiourea it follows that the active species reacting with these substances is* $Fe(CN)_5NO_2H^{3-}$ *formed as an unstable intermediate in the transition between the nitroprusside forms* $Fe(CN)_5NO^{2-}$ *and* $Fe(CN)_5NO_2^{4-}$*. The coloured products of these reactions are identical with those obtained by the photochemically induced reactions.*

## Introduction

Hitherto it has been known that the nitroprusside ion, $Fe(CN)_5NO^{2-}$, reacts with thiocyanate,[1] thiosulfate,[2] thiourea,[3] and aniline[4] under formation of coloured compounds when the aqueous reaction system is irradiated with moderate intensity light. Furthermore it has been found[5] that the observed reactions must result from the immediate products of excitation of $Fe(CN)_5NO^{2-}$. The resulting product *e.g.* in the $CNS^-$ case has been formulated as



$$\left[ Fe(CN)_5NO\begin{matrix} OH \\ CNS \end{matrix} \right]^{4-}$$

This is in contrast with conclusions of some other authors who report that the immediate products of the photodecomposition of $Fe(CN)_5NO^{2-}$ are NO and $Fe(CN)_5H_2O^{3-}$, or, that $Fe(CN)_5NO^{2-}$ is photoreduced in aqueous solution[6] to $Fe(CN)_5NO^{3-}$.

The present paper deals with our observation that the mentioned reactions proceed under certain conditions also without irradiation which makes it possible to draw conclusions about the basic character of the photo-induced reactions.

## Experimental Section

All chemicals used were Lachema products of p.a. purity grade. The nitroprusside in form of $Na_2Fe(CN)_5NO.2H_2O$ was recrystallized twice from water in darkness and its purity was checked polarographically.

The polarographic experiments were carried out on polarographs LP 60 and V-301 using the Kalousek vessel with external SCE. Spectrophotometric measurements were performed with the Uvispek spectrophotometer (Hilger-Watts).

## Results and Discussion

We have found that the same coloured products as resulting from the photochemical reactions mentioned in the Introduction are obtained without irradiation when a mixture of nitroprusside and one of the below quoted substances is alkalized to $pH>11$ and then acidified to $pH\leqslant4$. The important feature of these reactions is that they do not proceed at any constant pH value but only in the course of acidification of the alkaline reaction mixtures. This behaviour was observed with the following substances: $CNS^-$ (blue colour), $N_3^-$ (red-violet), thiourea (deep blue), $S_2O_3^{2-}$ (green-blue colour fading with time under deposition of elemental sulphur; in this respect this reaction differs from the other mentioned reactions which yield quite stable products). The same colourations are obtained with these substances when the neutral solutions are irradiated by the tungsten light. In case of $S_2O_3^{2-}$ the gree-blue colouration fades under deposition of sulphur by far not so quickly as after the acidification.

Figures 1 and 2 show the comparison of absorption spectra of solutions obtained by irradiation with tungsten light and by acidification of alkaline systems nitroprusside + $NaN_3$ and nitroprusside + KCNS, respectively. The similarity of both spectra suggests that in both cases the products are identical.

It is a well-known fact that the nitroprusside ion forms in alkaline media an equilibrium $Fe(CN)_5NO^{2-}+2OH^- \rightleftarrows Fe(CN)_5NO_2^{4-}+H_2O$ whereas the ratio 1:1 of both forms is attained[5,7] at pH round 11.5 depending on ionic strength and temperature. This

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(1) N. Tarugi, *Ann. Chem. Applic.*, *16*, 407 (1926); *17*, 519 (1927); *Chem. Abstr.*, *21*, 865 (1927).
(2) A. Casolari, *Rend. Soc. Chim. Ital.*, *5*, 294 (1914); *Chem. Abstr.*, *9*, 1435 (1915).
(3) O. Baudisch, *Science*, *108*, 443 (1948).
(4) V. G. Bělikov anl V. N. Bernštejn, *Sb. Naučn. Dokl.*, *38* (1960); *Chem. Abstr.*, *59*, 12182 (1963).
(5) J. H. Swinehart, *Coord. Chem. Rev.*, *2*, 385 (1967).
(6) W. P. Griffith, *Quart. Revs.*, *16*, 188 (1962).
(7) J. Mašek and J. Dempír, *Inorg. Chim. Acta*, *2*, 443 (1968).

means that the starting form of the nitroprusside in the reactions under consideration is always $Fe(CN)_5NO_2^{4-}$.

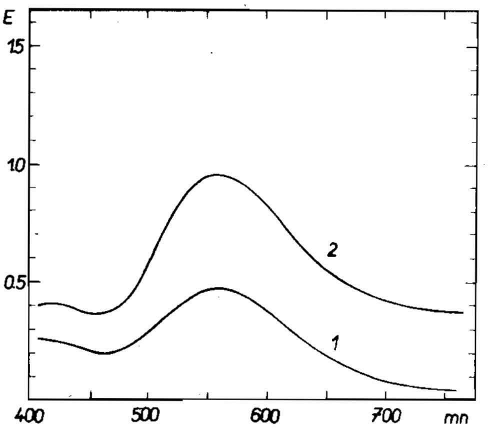


Figure 1. Absorption spectrum of the azide-nitroprusside complex. Curve 1: $4\times10^{-3}M$ $Na_2Fe(CN)_5NO+2\times10^{-1}M$ $NaN_3$ after irradiation with tungsten light for 4 hr. Curve 2: $4\times10^{-3}M$ $Na_4Fe(CN)_5NO_2+2\times10^{-1}M$ $NaN_3$ acidified with $H_2SO_4$ to pH ~ 4. 1 cm cell; slit 0.15 mm.

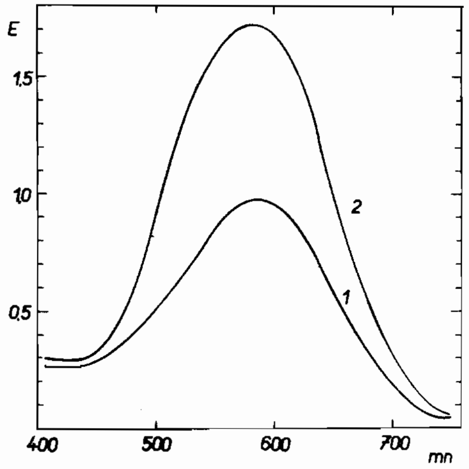


Figure 2. Absorption spectrum of the thiocyanate-nitroprusside complex. · Curve 1: $4\times10^{-3}M$ $Na_2Fe(CN)_5NO+2\times10^{-1}M$ KCNS after irradiation with tungsten light for 4 hr. Curve 2: $4\times10^{-3}M$ $Na_4Fe(CN)_5NO_2+2\times10^{-1}M$ KCNS acidified with $H_2SO_4$ to pH ~ 4. 1 cm cell; slit 0.15 mm.

The reaction proceeding on acidifying the system containing $Fe(CN)_5NO_2^{4-}$ and $CNS^-$ shows the following characteristics.

At the same $Fe(CN)_5NO_2^{4-}$ concentration the resulting colour is the more intensive the higher is the concentration of $CNS^-$. This indicates a relatively considerable dissociation of the resulting complex.

In order to develop the colour it is not sufficient to acidify the reaction mixture to the pH at which the transition $Fe(CN)_5NO_2^{4-} \rightleftarrows Fe(CN)_5NO^{2-}$ is accomplished, *i.e.* to pH about 10. At such a pH no colour develops. It is necessary to lower the pH to about 4 independently of the reaction partner.

When starting from different pH values on the dissociation curve of the system $Fe(CN)_5NO^{2-}/Fe(CN)_5NO_2^{4-}$ and acidifying to pH 4 in presence of $CNS^-$ then the curve expressing the dependence of intensity of the resulting colour on the starting pH is closely similar to the dissociation curve (Figure 3). This is a proof that the active substance formed during the acidification originates from the form $Fe(CN)_5NO_2^{4-}$.

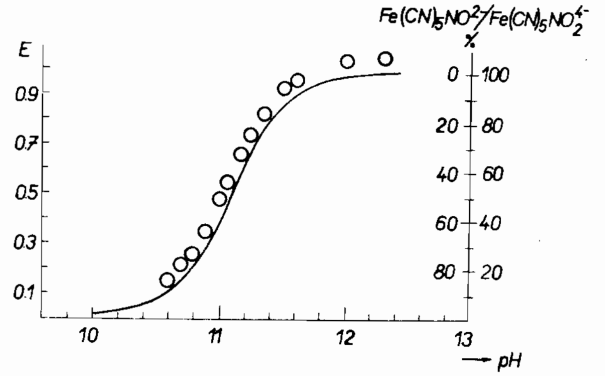


Figure 3. Dependence of the thiocyanate-nitroprusside complex absorbance on the starting pH in the acidification reaction. Circles denote absorbances of solutions obtained by acidifying to pH ~ 4 a mixture of $4\times10^{-3}M$ $Na_2Fe(CN)_5NO+2\times10^{-1}M$ KCNS in Britton-Robinson buffers of starting pH given by the abscissa. For comparison equilibrium concentration distribution of the forms $Fe(CN)_5NO^{2-}$ and $Fe(CN)_5NO_2^{4-}$ is given by the full line.

By the Job method the composition of the resulting complex was found to be nitroprusside: KCNS = 1 : 1. The shape of the Job curves indicates also a considerable dissociation of the resulting complex.

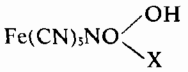
In order to check if the active species reacting with $CNS^-$ is not $Fe(CN)_5H_2O^{3-}$ formed[8] in alkaline solution from $Fe(CN)_5NO_2^{4-}$ the alkaline nitroprusside solution was irradiated for 15 minutes by UV light which causes a total conversion[9] of $Fe(CN)_5NO_2^{4-}$ to $Fe(CN)_5H_2O^{3-}$. The resulting solution was acidified and KCNS added. No colouration developed similarly as in the case that the acidification was carried out with the KCNS already added. These results show that the active species cannot be the decomposition products of $Fe(CN)_5NO_2^{4-}$ in alkaline media.

All the described results can be interpreted by assuming that the active species reacting with $CNS^-$ or other mentioned substances is $Fe(CN)_5NO_2H^{3-}$ which is the intermediate of the transition $Fe(CN)_5NO^{2-}$ to $Fe(CN)_5NO_2^{4-}$ and back. From a detailed analysis of kinetics of the system $Fe(CN)_5NO^{2-} \overset{1}{\rightleftarrows} Fe(CN)_5NO_2^{3-} \overset{2}{\rightleftarrows} Fe(CN)_5NO_2^{4-}$ it can be shown[7] that the equilibrium 2 is established instantaneously (in the order of μsec) and its pK is situated at lower pH values than that of the equilibrium 1 which is established slowly (in the order of sec). From these properties of the system is follows that when alkalizing a solution containing the form $Fe(CN)_5NO^{2-}$ the

(8) J. H. Swinehart and P. A. Rock, *Inorg. Chem.*, 5, 573 (1966).
(9) F. Feigl, Quantitative Analyse mit Hilfe von Tüpfelreaktionen, 3rd ed., p. 420, Akademische Verlagsgesellschaft, Leipzig (1938).

species $Fe(CN)_5NO_2H^{3-}$ appears in the course of the reaction in a negligible steady-state concentration which has no chance to react with $CNS^-$ or other reaction partners and moreover there is a strong competition in the reaction with the second $OH^-$ ion. On the other hand, when the solution containing the species $Fe(CN)_5NO_2^{4-}$ is acidified well below the pK of the equilibrium 2 then the species $Fe(CN)_5NO_2H^{3-}$ appears immediately in a concentration practically equal to that of $Fe(CN)_5NO_2^{4-}$ in the initial solution, and is converted slowly to $Fe(CN)_5NO^{2-}$. During this reaction it can react with $CNS^-$ or other reaction partners and be thus stabilized against the conversion to $Fe(CN)_5NO^{2-}$. This explains the unusual property of the colour reactions which proceed only during the acidification of the alkaline nitroprusside solution, and also the similar shape of the curves in Figure 3.

These results throw also a new light on the nature of the photochemical reactions of the nitroprusside ion. It is known[10] that irradiation of the neutral $Fe(CN)_5NO^{2-}$ solutions results in a pH decrease, which increases to nearly the original value when irradiation ceases. Thus it seems that the irradiation facilitates a formation of $Fe(CN)_5NO_2H^{3-}$ and stabilizes it so that in presence of $CNS^-$ or other described ligands the same reaction occurs as when acidifying the alkaline mixtures. Therefore the structure



$$Fe(CN)_5NO\begin{matrix}\nearrow OH\\ \searrow X\end{matrix}$$

(where X denotes $CNS^-$, $N_3^-$ or other mentioned substances) seems to be correct for the coloured products and it would be misleading to derive their structure from $Fe(CN)_5H_2O^{3-}$ or $Fe(CN)_5NO^{3-}$ which are reported as irradiation products of the nitroprusside ion.[3,6,11-13]

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(10) R. P. Mitra, D. V. S. Jain, A. K. Banergie, and K. V. R. Chari, *J. Inorg. Nucl. Chem.*, *25*, 1263 (1963).

(11) J. Danon, P. A. Muniz, and H. Panapucci, *J. Chem. Phys.*, *41*, 3651 (1964).

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(13) D. A. C. McNeil, J. B. Raynor, and M. C. R. Symons, *Proc. Chem. Soc.*, 364 (1964).