

PHOTOCHEMICAL REACTION INVOLVING NITROSYL PENTACYANOFERRATE (II) SYSTEM

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ABSTRACT

Sodium nitroprusside contains cyanide ligand that cannot be so easily replaced chemically. An effort has been made to substitute this photochemical reaction like selenite. The rate of this photochemical reaction has been observed spectrophotometrically. The effect of different parameters like pH, light intensity, effect of sodium nitroprusside and selenite ligand concentration on the rate of this substitution reaction has been studied. Product was isolated and characterized. A tentative mechanism for this photochemical substitution reaction has been proposed.

Key words: Sodium nitroprusside, Sodium selenite, Photochemical ligand substitution reaction.

INTRODUCTION

Aqueous solution of sodium nitroprusside undergoes a complex decomposition process in the presence of light¹. A number of workers have reported the photosensitivity of aqueous solution of nitroprusside in the nineteenth century, but unfortunately the results reported are contradictory with one another. It may be due to the probable failure to distinguish between primary photochemical reaction and secondary photochemical and/or thermal processes as well as control reaction conditions during irradiation. When aqueous² or acidic³ solutions of the sodium nitroprusside were exposed to diffused daylight, it was reported that nitric oxide was produced. Prussian blue was precipitated in this solution on long exposure. Mitra et al.⁴ reported that initially a reversible reaction takes place on exposure of aqueous solution of $[\text{Fe}(\text{CN})_5(\text{NO})]^{2-}$ with uv light. This reaction involves the production of weak acid. On prolonged irradiation, secondary reactions occur with the appearance of a dark blue colour and the reaction becomes irreversible from pH point of view. The dark blue colour was proposed to be due to the formation of some ferrous nitrites. Lal⁵ observed that an aqueous solution of

$[\text{Fe}(\text{CN})_5(\text{NO})]^{2-}$ was converted into $[\text{Fe}(\text{CN})_5(\text{H}_2\text{O})]^{2-}$ on irradiation in the presence of hydrogen peroxide. A blue product was also reported, when this reaction was carried out in the presence of thiourea² and thiocyanate⁶. This blue product was proposed to be $[\text{Fe}(\text{CN})_5(\text{H}_2\text{O})]^{2-}$.

Van Voorst and Hemmerich⁷ investigated the chemical reduction of nitroprusside solution in water and also in N, N-dimethyl formamide and reported that, the nature of reduced product depends on the acidity of the medium. The products have been tentatively assigned the structures as $[\text{Fe}(\text{CN})_5(\text{NO})]^{3-}$ or $[\text{Fe}(\text{CN})_5(\text{NO})]^{2-}$. The exchange reaction between $[\text{Fe}(\text{CN})_5(\text{NO})]^{2-}$ and CN^- ions is claimed to be photocatalysed⁸. The cyanide ligand trans to the NO group was reported to have a preferential exchange⁹. Reactions of thiourea with nitroprusside gave a red colored adduct, which is gradually converted into a blue product¹⁰. Similar reaction was also shown by aqueous thiocyanate¹¹. The formation of a hydroxo complex $[\text{Fe}(\text{CN})_5(\text{OH})]^{4-}$, NO^{2-} and $[\text{Fe}(\text{CN})_5(\text{H}_2\text{O})]^{3-}$ has been reported by Sahasi¹² in photocatalytic reaction of sodium nitroprusside on some semiconducting oxides. Photochemical generation of nitroprusside induced by MLCT excitation in aqueous solution at room temperature was reported by Song and Lin¹³. The photometric determination of thiourea with the use of sodium nitroprusside was presented by Anisimova et al.¹⁴

A critical survey of the literature reveals that the photochemistry of sodium nitroprusside has received negligible attention¹⁵. Ameta et al.¹⁶ have reported the photochemical ligand exchange reactions of sodium nitroprusside by using metabisulphite ions and bicarbonate ions. The photochemical reaction of sodium nitroprusside may be useful to have an insight in the understanding of its photochemical behaviour on one hand and it will also provide some alternate routes to prepare some newer complexes on the other. The present work describes the photochemical reaction of pentacyanonitrosyl ferrate (II), $[\text{Fe}(\text{CN})_5(\text{NO})]^{2-}$, in the presence of selenite ligands.

EXPERIMENTAL

Sodium nitroprusside and sodium selenite were used in present investigation. 0.3020 g. of sodium nitroprusside and 0.1710 g. of sodium selenite were dissolved in 100 mL doubly distilled water and was exposed to a 200 W tungsten lamp (Philips; light intensity = 14.0 mWcm^{-2}). The light intensity was measured with the help of a solarimeter (Suryamapi Model EL 201). A water filter was used to cut off the thermal radiations. A digital pH meter (Systronics Model 324) measured the pH of the solution. The desired pH of the solution was adjusted by the addition of previously standardised sulphuric acid and sodium hydroxide solutions.

The progress of the photochemical reaction was observed by taking absorbance at regular time intervals using spectrophotometer (JASCO UV 7800). Estimation of Fe, Na, Se in the products were made on Atomic Absorption Spectrometer (Varian Techtron - AA - 6D) and the

estimation of carbon, hydrogen and nitrogen were made on CARLO ERBA - 1106 microanalyser.

RESULTS AND DISCUSSION

An aliquot of 5.0 mL was taken out from the reaction mixture and the change in absorbance was observed at $\lambda_{\text{max}} = 660 \text{ nm}$ with time of exposure.

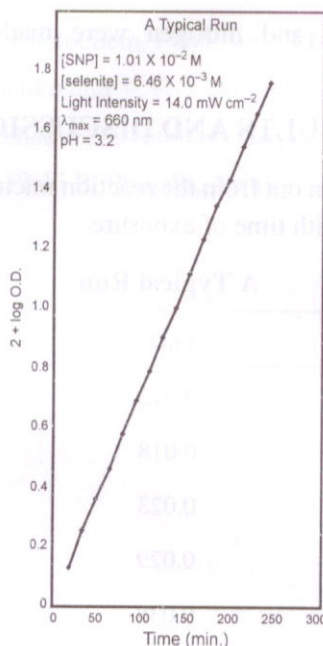
A Typical Run

Time	O.D.	2 + log O.D.
15.0	0.013	0.1280
30.0	0.018	0.2553
45.0	0.023	0.3617
60.0	0.029	0.4624
75.0	0.038	0.5798
90.0	0.049	0.6902
105.0	0.062	0.7924
120.0	0.082	0.9031
135.0	0.100	1.0000
150.0	0.130	1.1139
165.0	0.170	1.2304
180.0	0.22	1.3424
195.0	0.27	1.4314
210.0	0.35	1.5441
225.0	0.45	1.6532
240.0	0.57	1.7559

It was observed that a plot of log (absorbance) v/s time was linear and it followed pseudo - first order kinetics. The rate constant of the reaction has been calculated by the expression

$$k = 2.303 \times \text{Slope.}$$

The results are graphically shown in Figure - 1.



Effect of pH

The photochemical reaction of sodium nitroprusside in presence of selenite ligand may be affected by the pH values and, therefore, the effect of pH on this photochemical reaction has been investigated. The results are reported in Table 1.

TABLE 1
EFFECT OF pH

[SNP] = 1.01×10^{-2} M		[Selenite] = 6.46×10^{-3} M
Light Intensity = 14.0 mW cm^{-2}		λ_{max} = 660 nm
pH	$k \times 10^2 (\text{min}^{-1})$	
1.5	1.13	
2.0	1.25	
2.5	1.42	
3.2	1.65	
3.5	1.56	
4.0	1.42	
5.0	1.20	
6.5	0.81	
7.0	0.61	
8.0	0.44	

It was observed that the rate of this ligand exchange reaction increases on increasing the pH of the reaction medium. It reaches a maximum at pH = 3.2. A decrease in the rate of this reaction was observed on increasing pH further. It may be explained on the basis that as the pH was increased, the availability of the ligand ion increases in its anionic form SeO_3^{2-} and hence, the reaction rate increases. But on increasing the pH above 3.2, there is a possibility of a competitive reaction of ligand ions, SeO_3^{2-} with that of OH^- ions. Thus, a corresponding decrease in the rate of reaction was observed.

Effect of Sodium Nitroprusside Concentration

The effect of the sodium nitroprusside on the rate of photochemical reaction was observed. The results are reported in Table 2.

TABLE 2
EFFECT OF SNP CONCENTRATION

[Selenite] = 6.46×10^{-3} M

Light Intensity = 14.0 mWcm^{-2}

pH = 3.2

$\lambda_{\text{max}} = 660 \text{ nm}$.

[Sodium Nitroprusside] $\times 10^2$ M	$k \times 10^2 (\text{min}^{-1})$
0.80	1.15
0.84	1.26
0.88	1.33
0.91	1.37
0.94	1.45
0.98	1.55
1.01	1.65
1.04	1.57
1.07	1.50
1.09	1.45
1.11	1.41
1.15	1.33
1.19	1.25

It has been observed that the rate of photochemical reaction of sodium nitroprusside with selenite ions increases with an increase in the concentration of sodium nitroprusside. This may be due to the fact that as the concentration of sodium nitroprusside was increased, the number of excited species also increase; thus, resulting into a corresponding increase in the rate of reaction. After a certain limit, if the concentration of sodium nitroprusside was further

increased, there was a decrease in the rate of the reaction. This decrease may be explained on the basis that the substrate is dark red coloured, it will absorb a major part of incident radiation and, therefore, there will be a decrease in the rate of reaction mixture. In other words, the solution of nitroprusside will start acting like a filter and as a consequence, the reaction rate was found to decrease.

Effect of Selenite Concentration

The effect of concentration of selenite on rate of photochemical reaction of sodium nitroprusside was also observed by taking different concentration of selenite. The results are summarised in Table 3.

TABLE 3
EFFECT OF SELENITE CONCENTRATION

[SNP] = 1.01×10^{-2} M Light Intensity = 14.0 mW cm^{-2}
pH = 3.2 $\lambda_{\text{max}} = 660 \text{ nm}$

[Selenite] $\times 10^3$ M	$k \times 10^2 \text{ (min}^{-1}\text{)}$
3.80	1.11
4.18	1.25
4.56	1.33
4.94	1.41
5.30	1.48
5.70	1.54
6.08	1.59
6.46	1.65
6.84	1.60
7.22	1.55
7.60	1.46
7.98	1.40
8.36	1.32
8.7	1.27

It was observed that as the concentration of sodium selenite was increased, there was a corresponding increase in the rate of reaction, reaching a maximum at $[\text{Na}_2\text{SeO}_3] = 6.46 \times 10^{-3}$ M. It may be explained on the basis of the fact that the reaction rate increases due to increase in the concentration of participation species. On the other hand, a decrease in the rate of the

reaction was observed on increasing the concentration of sodium selenite above 6.46×10^{-3} M. It may be attributed to the fact that higher concentration of selenite ions may hinder its own movement to reach the excited species of sodium nitroprusside in a desired time limit. Thus, a decrease in the rate of the reaction was observed for higher concentration of selenite ions.

Effect of Light Intensity

The effect of intensity of light on the rate of photochemical reaction of sodium nitroprusside has been observed by varying the distance between the exposed surface of the reaction mixture and the source. The results are tabulated in Table 4. The results indicate that reaction rate is accelerated as the intensity of light was increased. This may be due to the fact that any increase in the light intensity will increase the number of photons striking per unit area of the reaction mixture. After a certain limit i.e., $I = 14.0 \text{ mW cm}^{-2}$, no reasonable increase in the rate of reaction has been observed. Rather, it reaches a saturation point at a particular intensity. It suggests that further increase in the light intensity will not increase the rate of this photochemical reaction any more, as the surface of the reaction mixture remains fixed.

TABLE 4
EFFECT OF LIGHT INTENSITY

[SNP] = 1.01×10^{-2} M		[Selenite] = 6.46×10^{-3} M	
pH = 3.2		$\lambda_{\text{max}} = 660 \text{ nm}$	
Intensity of light (mW cm^{-2})		$k \times 10^2 (\text{min}^{-1})$	
6.0		1.14	
7.0		1.22	
8.0		1.29	
9.0		1.35	
10.0		1.41	
11.0		1.46	
12.0		1.52	
13.0		1.57	
14.0		1.65	
15.0		1.65	
16.0		1.65	
17.0		1.65	
18.0		1.65	

An effort was made to know the requirement of light in different steps of this reaction. It was observed that the reaction stops at a particular step, as soon as the light source was cut off. The reaction reaches its completion only, when the light exposure was continued through out the progress of the reaction.

Product Analysis

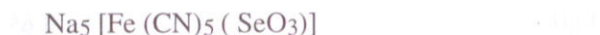
In neutral medium, the photochemical reaction between nitroprusside and selenite was carried out. It was observed that the initial light red colour of the reaction mixture changes to yellow. The reaction was allowed to proceed to completion and then it was filtered. The filtrate was evaporated on a water bath. The product was separated by fractional crystallisation. It was recrystallised with methanol giving yellow crystals of the product, which was analysed as follows -

(1) Elemental Analysis :

Element	Found	Calculated
Na	26.40 %	26.86 %
Fe	13.17 %	13.08 %
C	13.90 %	14.02 %
N'	16.40 %	16.36 %
Se	17.96 %	18.46 %

(2) UV (water) - $\lambda_{\max} = 530 \text{ nm}$

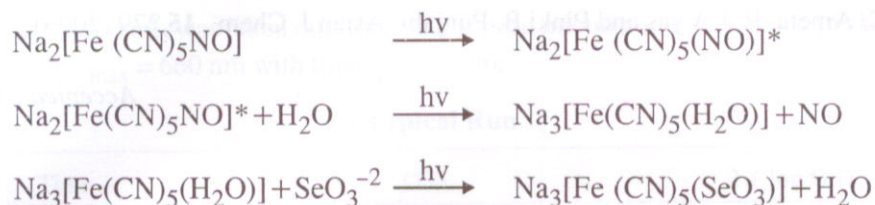
(3) IR (KBr) - A comparison of the i.r. spectra of the sodium nitroprusside, sodium selenite and the product clearly indicates the removal of nitrosyl ligand from the coordination sphere of the iron. The characteristic bands of NO^+ ligand at 1944 and 670 cm^{-1} were found absent in the i.r. spectrum of the product. It has been observed that selenite ion has characteristic bands at 1130 and 990 cm^{-1} . It was observed that bands at 1120 and 985 cm^{-1} also appeared in the i.r. spectrum of the product. These bands may be attributed to the presence of O-bonded selenite ligand to the central metal ion. On the basis of the spectral and analytical data, the following tentative structure have been proposed for the compound.



In this case, selenite behaves as a unidentate ligand used for removing one NO^+ ligand from the coordination sphere of the sodium nitroprusside complex. A positive test for nitrite ion in the solution has been observed, which indicates the removal of NO^+ .

MECHANISM

On the basis of the experimental observations, a tentative mechanism for this photochemical ligand exchange reaction of sodium nitroprusside has been proposed as -



Initially, the sodium nitroprusside is excited by absorbing incident radiations of desired wavelength. Then its excited state will react with water and as a consequence, water enters the coordination sphere of iron, replacing nitrosylium ion (NO^+). This exchange is energetically favourable, because neutral ligand (H_2O), can replace cationic ligand (NO^+). Now, selenite ions can easily throw water molecules out of the coordination sphere of iron as anionic ligand can replace a neutral ligand.

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