Ligand exchange reactions of sodium nitroprusside in the presence of sulphate ion under photochemical conditions

Mayank R Mehta, Piyush J Vyas, Jitendra Vardia & Suresh C Ameta*

Department of Chemistry, College of Science, Sukhadia University, Udaipur (Raj.) 313002, India

Received 6 November 2001; revised 25 February 2003

Sodium nitroprusside contains cyanide ligands that are not easily replaced chemically. An effort has been made to substitute this ligand by another anionic ligand like sulphate. The rate of this photochemical reaction has been observed spectrophotometrically. The effects of different parameters like pH, light intensity, concentration of sodium nitroprusside and sulphate ligand concentration on the rate of this substitution reaction have been studied. The product is isolated and characterized. A tentative mechanism for this photochemical substitution reaction has been proposed.

Aqueous solution of sodium nitroprusside undergoes a complex decomposition process in the presence of light. The results reported are contradictory with one another. Van Voorst and Hemmerich investigated the chemical reduction of nitroprusside solution in water and also in N, N-dimethylformamide and reported that the nature of reduced product depends on the acidity of the medium. The products have been tentatively assigned the structures as [Fe(CN)₅(NO)]²⁻ or [Fe(CN)₅(OH)]²⁻. The exchange reaction between [Fe(CN)₅(NO)]²⁻ and CN⁻ ions is claimed to be photocatalysed. The cyanide ligand trans to the NO group was reported to have a preferential exchange. Reactions of thiourea with nitroprusside gave a red coloured adduct, which is gradually converted into a blue product. Similar reaction was also shown by aqueous thiocyanate. The formation of a hydroxo complex [Fe(CN)₅(OH)]⁴⁻, NO₂⁻ and [Fe(CN)₅(H₂O)]³⁻ has been reported by Sahasi in photocatalytic reaction of sodium nitroprusside on some semiconducting oxides. Song and Lin reported photochemical generation of nitroprusside induced by MLCT excitation in aqueous solution at room temperature. The photometric determination of thiourea with the use of sodium nitroprusside was presented by Anisimova et al.

A critical survey of the literature reveals that the photochemistry of sodium nitroprusside has received negligible attention. 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), [Fe(CN)₅(NO)]²⁻, in the presence of sulphate ligands.

Experimental

Sodium nitroprusside (EM) and sodium sulphate (SDS) were used in present investigation. 0.3188 g of sodium nitroprusside and 0.2948 g of sodium sulphate were dissolved in 100 mL doubly distilled water and was exposed to a 200 W tungsten lamp (Philips; light intensity = 13.0 mW cm⁻²). The light intensity was measured with the help of a solarimeter (Suryamani Model CEL 201). A water filter was used to cut off the thermal radiations. A digital pH meter (Systronics Model 324) was used to measure the pH of the solution. The desired pH of the solution was adjusted by adding previously standardized 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 and Na in the products were made on atomic absorption spectrometer (Varian Techtron-AA-6D) and the estimation of carbon, hydrogen, nitrogen and sulphur 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 λmax = 620 nm with time of exposure. 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 = 2.303xslope.

The rate constant was found to be 1.28x10⁻² min⁻¹ (under the following experimental conditions: [SNP] = 1.07x10⁻⁷M, [Sulphate] = 9.15x10⁻³M, pH = 2.8 and light intensity = 13.0 mW cm⁻²).

The photochemical reaction of sodium nitroprusside in presence of sulphate ligand may be affected by the pH values and, therefore, the effect of
on this photochemical reaction has been investigated. 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 = 2.8. A decrease in the rate of this reaction was observed on increasing pH further. It is observed that as the pH increases, the availability of the ligand ion increases in its anionic form SO₄²⁻ and hence, the reaction rate increases. But, on increasing the pH above 2.8, there is a possibility of a competitive reaction of ligand ions, SO₄²⁻ with that of OH⁻ ions. Thus, a corresponding decrease in the rate of reaction is observed. Thus pH = 2.8 was used for all further studies.

The effect of the concentration of sodium nitroprusside ranging from 0.97x10⁻³ M to 1.17x10⁻² M on the rate of photochemical reaction was observed. It has been observed that the rate of photochemical reaction of sodium nitroprusside with sulphate ions increases with an increase in the concentration of sodium nitroprusside up to 1.07x10⁻² M. This may be due to the fact that as the concentration of sodium nitroprusside is increased, the number of excited species also increase; thus, resulting in corresponding increase in the rate of reaction. After 1.07x10⁻² M, 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, which will absorb a major part of incident radiation travelling through the reaction mixture and, therefore, there will be a decrease in the light intensity reaching sodium nitroprusside in the bulk of reaction mixture. In other words, the solution of nitroprusside will start acting as a filter and as a consequence, the reaction rate was found to decrease. Therefore, sodium nitroprusside concentration chosen for all further studies was 1.07x10⁻² M.

The effect of concentration of sulphate on the rate of photochemical reaction of sodium nitroprusside was also observed by taking different concentration of sulphate ranging from 7.04x10⁻³ M to 11.26x10⁻² M. It was observed that as the concentration of sodium sulphate was increased, there was a corresponding increase in the rate of reaction, reaching a maximum at [Na₂SO₄] = 9.15x10⁻³ M. It can be explained on the basis of the fact that the reaction rate increases due to increase in the concentration of participating species. On the other hand, a decrease in the rate of the reaction was observed on increasing the concentration of sodium sulphate above 9.15x10⁻³ M. It may be attributed to the fact that higher concentrations of sulphate 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 concentrations of sulphate ions. Thus a concentration of 9.15x10⁻³ M of sulphate was chosen for all further studies.

The effect of intensity of light on the rate of photochemical reaction of sodium nitroprusside was observed by varying the distance between the exposed surface of the reaction mixture and the source. It was found that the reaction rate is accelerated as the intensity of light was increased from l = 6.0 mWcm⁻². 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., l = 13.0 mWcm⁻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.

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 throughout the progress of the reaction.

**Product analysis**

In neutral medium, the photochemical reaction between nitroprusside and sulphate was carried out. It was observed that the initial light red colour of the reaction mixture changes to peacock blue. The reaction was allowed to proceed to completion and then it was filtered. The filtrate was evaporated on a water bath and the residue was recrystallised with methanol giving green crystals of the product, which was analyzed. Elemental analysis was carried out. (Found) Fe = 12.00%, C = 9.80%, N = 11.50%, S = 13.00% and Na = 28.00%. (Calculated) Fe = 11.60%, C = 9.77%, N = 11.40%, S = 13.03% and Na = 28.10%. UV (water) – λmax was found to be 520nm. A comparison of the IR spectra of the sodium nitroprusside, sodium sulphate 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 660 cm⁻¹ were found absent in the IR spectrum of the product. It is known that sulphate ion has characteristic bands at 1120 and
It was observed that bands at 1110 and 980 cm\(^{-1}\) also appeared in the IR spectrum of the product. These bands may be attributed to the presence of S-bonded sulphate ligand to the central metal ion.

The test of CN\(^{-}\) ions was found positive in solution. On the basis of the spectral and analytical data, the following tentative structure has been proposed for the compound.

\[ \text{Na}_6[\text{Fe(CN)}_4(\text{SO}_4)_2] \]

In this case sulphate behaves as a unidentate ligand. Two sulphate ions have been used for replacing one CN\(^{-}\) and one NO\(^{+}\) ligand from the coordination sphere of the sodium nitroprusside complex.

**Mechanism**

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

\[
\begin{align*}
\text{Na}_2[\text{Fe(CN)}_3\text{NO}] & \xrightarrow{\text{hv}} \text{Na}_2[\text{Fe(CN)}_3\text{NO}]^* \\
\text{Na}_2[\text{Fe(CN)}_3\text{NO}]^* + \text{H}_2\text{O} & \xrightarrow{\text{hv}} \text{Na}_3[\text{Fe(CN)}_5(\text{H}_2\text{O})] + \text{NO}^{+} \\
\text{Na}_3[\text{Fe(CN)}_5(\text{H}_2\text{O})] + \text{SO}_4^{2-} & \rightarrow \text{Na}_5[\text{Fe(CN)}_5(\text{SO}_4)] + \text{H}_2\text{O} \\
\text{Na}_5[\text{Fe(CN)}_5(\text{SO}_4)] + \text{SO}_4^{2-} & \rightarrow \text{Na}_6[\text{Fe(CN)}_4(\text{SO}_4)_2] + \text{CN}^- 
\end{align*}
\]

Initially, the sodium nitroprusside is excited by absorbing incident radiations of desired wavelength. Then its excited state reacts with water and as a consequence, water enters the coordination sphere of iron, replacing nitrosylum ion (NO\(^{+}\)). This exchange is energetically favorable, because neutral ligand (H\(_2\)O), can replace cationic ligand (NO\(^{+}\)). Now sulphate ions can easily throw water molecules out of the coordination sphere of iron as anionic ligand can replace a neutral ligand. In the last step, another sulphate ion (a weaker ligand) pushes cyanide ion (a stronger ligand) as evident from the chemical analysis of the product.

These ligand exchange reactions are well known in the field of coordination chemistry, but these reactions ordinarily involve the substitution of a weaker ligand by a stronger ligand. Such reactions are both, thermodynamically and kinetically, favorable. It does not seem feasible to have reverse exchange i.e. substituting a stronger ligand by a weaker ligand. The present work not only provides a pathway for this unfavorable reaction, but also opens further avenues for such photochemical ligand exchange reactions.

**Acknowledgement**

The authors are grateful to R & D department, IFFCO, Kalol (North Gujarat) for estimation of Fe and Na and RSIC, Chandigarh for elemental analysis.

**References**