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PHOTOCHEMICAL LIGAND EXCHANGE REACTION INVOLVING SODIUM NITROPRUSSIDE – MALONIC ACID SYSTEM

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ABSRACT

$Na_2[Fe(CN)_5NO]. 2H_2O$ contains cyanide ligands that cannot be so easily replaced chemically. An effort has been made to substitute this ligand by another anionic ligand like malonate (bidentate ligand). The progress of this photochemical reaction has been observed spectrophotometrically and the product was isolated and characterized. The effects of different parameters like pH, intensity of light concentration of sodium nitroprusside and ligand concentration on the yield of this substitution product have been studied. A tentative mechanism for this reaction has been proposed.

Key words : Sodium nitroprusside, Malonic acid, Photochemical, Substitution reaction.

INTRODUCTION

Aqueous solution of sodium nitroprusside undergoes a complex decomposition process in the presence of light[1]. A number of researchers have reported the photosencitivity of aqueous solution of nitroprusside in the nineteenth century, but unfortunately the results reported are contradictory with one another. Mitra et al. [2] reported that initially a reversible reaction take place on exposure of aqueous solution of $[Fe(CN)_5NO]^{2-}$ with u. v. light. Lal[3] observed that an aqueous solution of $[Fe(CN)_5NO]^{2-}$ was converted into $[Fe(CN)_5(H_2O)]^{2-}$ on irradiation in the presence of hydrogen peroxide.

Van Voorst and Hemmerich[4] 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 exchange reaction between

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$[Fe(CN)_5NO]^{2-}$ and CN^- ions is claimed to be photocatalysed[5]. The cyanide ligand trans to the NO group was reported to have a preferential exchange[6]. Reaction of thiourea with nitroprusside gave a red coloured adduct, which is gradually converted into a blue product[7]. Similar reaction was also shown by aqueous thiocyanate[8]. The formation of a hydroxo complex $[Fe(CN)_5(OH)]^{4-}$, NO_2^- and $[Fe(CN)_5(H_2O)]^{3-}$ has been reported by Sahasi[9] 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 Lin[10]. The photometric determination of thiourea with the use of sodium nitroprusside was presented by Anisimova et al. [11]. Photochemical reactions have been exploited to yield coordination compounds, which are otherwise difficult to be prepared[12]. Photosubstitution reactions are also employed in the synthesis of a large number of $[RuX(bipy)_2L]^+$ and $[RuX(bipy)_2]$ complexes[13].

A critical survey of the literature reveals that the photochemistry of sodium nitroprusside has received negligible attention[14]. 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 route to prepare some newer complexes on the other. The present work describes the photochemical reaction of pentacyanonitrosyl ferrate (II), $[Fe(CN)_5NO]^{2-}$, in the presence of bidentate ligand like malonate.

EXPERIMENTAL

The stock solution of malonic acid was prepared in doubly distilled water. 0.065 g and 0.030 g of sodium nitroprusside (SNP) and malonic acid were dissolved in 25 mL of distilled water, respectively and these were mixed in a 100 mL beaker. Then this solution was exposed to sunlight (light intensity = 160.0 $mWcm^{-2}$). The light intensity was measured by a solarimeter (Suryamapi 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 addition of previously standardized sulphuric acid and sodium hydroxide solutions. Then this solution was exposed to a 200 W tungsten lamp. Similar reaction mixtures were prepared and these were exposed to a mercury lamp and sunlight, respectively.

The reaction was allowed to reach its completion and then, the reaction mixture was filtered. The filtrate was evaporated on a water bath and the residue was obtained by proper washing and drying. The yield was measured by a digital balance.

Effect of pH

The photochemical reaction of sodium nitroprusside in presence of malonic acid (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] = 4.36×10^{-3} M

[Malonic Acid] = 5.76×10^{-3} M

Light Intensity :
Hg and W-lamp = 16.0 $mWcm^{-2}$
Sunlight = 160.0 $mWcm^{-2}$

pH	Yield x 10^2 g		
	Sun light	W-Lamp	Hg-Lamp
2.0	6.4	4.2	2.6
2.5	7.1	5.7	3.9
3.0	9.0	7.2	6.0
3.5	7.9	6.2	4.4
4.0	7.2	5.2	3.4
4.5	6.7	4.5	2.3
5.0	6.2	3.2	1.8
5.5	5.3	2.5	1.6
6.0	4.6	1.7	1.3
7.0	4.1	1.5	1.0
7.5	3.5	1.2	0.8

It was observed that the yield of this ligand exchange reaction increases on increasing the pH of the reaction medium. It reaches a maximum at pH = 3.0. A decrease in the yield of the product 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 in its anionic form $C_3H_2O_4^{-2}$ increased and hence, the yield of the product also increases. But, on increasing the pH above 3.0, there is a possibility of a competitive reaction of ligand ions, $C_3H_2O_4^{-2}$ with that of OH^- ions and thus, a corresponding decrease in the yield was observed.

Effect of sodium nitroprusside concentration

Table 2 : Effect of concentration of sodium nitroprusside

pH = 3.0

[Malonic Acid] = 5.76×10^{-3}M

Light Intensity :
Hg and W-lamp = 16.0 $\mathrm{mWcm^{-2}}$
Sunlight = 160.0 $\mathrm{mWcm^{-2}}$

[SNP] x 10^3 M	**Yield x 10^2 g**		
	Sun light	**W-Lamp**	**Hg-Lamp**
0.67	5.2	2.9	1.6
1.01	5.9	3.5	1.9
1.34	6.5	4.5	2.2
1.68	6.9	5.1	2.5
2.01	7.2	5.4	2.8
2.35	7.6	5.8	3.2
2.69	7.8	5.9	3.5
3.02	8.1	6.2	3.8
3.36	8.3	6.4	4.1
3.69	8.5	6.7	4.4
4.03	8.7	6.9	5.2
4.36	9.0	7.2	6.0
4.70	8.5	5.9	4.2
5.03	7.2	5.3	3.6
5.37	6.5	3.7	2.5
5.71	5.2	2.9	1.7

The effect of the concentration of sodium nitroprusside on the yield of product was observed, by keeping all other factors identical. The range of concentration was kept between 0.67×10^{-3} M to 5.71×10^{-3} M. The results are reported in Table 2.

It has been observed that the yield of the product of sodium nitroprusside with malonic acid 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 increases; thus, resulting into a corresponding increase in the yield. After a certain limit of concentration, i. e. 4.36 x 10^{-3} M, if the concentration of sodium nitroprusside was further increased, there was a decrease in the yield of the product.

This decrease may be explained on the basis that the substrate is dark red coloured, which will absorb a major part of incident radiations travelling through the reaction mixture and, therefore, there will be a decrease in the light intensity reaching sodium nitropusside in the bulk of reaction mixture. In other words, the solution of nitroprusside will start acting as a filter and as a consequence, the yield was found to decrease.

Effect of malonic acid concentration

Table 3 : Effect of concentration of malonic acid

pH = 3.0

[SNP] = 4.36 x 10^{-3} M

Light Intensity :
Hg and W-lamp = 16.0 mWcm^{-2}
Sunlight = 160.0 mWcm^{-2}

[Malonic Acid] x 10^3 M	Yield x 10^2 g		
	Sun light	W-Lamp	Hg-Lamp
0.96	5.8	2.7	1.5
1.92	6.4	3.3	2.0
2.88	6.9	4.2	3.0
3.84	7.7	5.3	4.0
4.80	8.6	6.4	5.0
5.76	9.0	7.2	6.0
6.73	8.8	6.8	5.0
7.69	8.5	5.3	4.5
8.65	8.0	4.8	4.0
9.61	7.5	3.7	3.0
10.57	6.8	3.1	2.5

The effect of concentration of malonic acid on the yield of product was also observed by taking different concentrations of malonic acid, keeping all other factors identical. The results are reported in Table 3.

It was observed that as the concentration of malonic acid was increased, there was a corresponding increase in the yield of product reaching a maximum at [Malonic acid] = 5.76×10^{-3} M. It can be explained on the basis of the fact that the yield increases due to an increase in the concentration of participating species. On the other hand, a decrease in the yield was observed on increasing the concentration of malonic acid above 5.76×10^{-3} M. It may be attributed to the fact that higher concentration of malonic acid may hinder its own movement to reach the excited species of sodium nitroprusside in a desired time limit. Thus, a decrease in the yield of the product was observed for higher concentrations of malonic acid.

Effect of light intensity

The effect of light intensity on the yield of product has been observed by varying the distance between the exposed surface of the reaction mixture and the light source. The results for tungsten lamp and mercury lamp are tabulated in Table 4(a) and the results for sunlight are tabulated in Table 4(b).

Table 4(a) : Effect of light intensity

pH = 3.0 [Malonic Acid] = 5.76×10^{-3} M

[SNP] = 4.36×10^{-3} M

Intensity of light ($mWcm^{-2}$)	Yield x 10^2 g	
	W-Lamp	**Hg-Lamp**
6.0	2.8	2.1
7.0	3.4	2.5
8.0	4.0	2.9
9.0	4.5	3.3
10.0	5.0	3.7
11.0	5.3	4.1
12.0	5.6	4.5
13.0	6.0	5.0
14.0	6.3	5.4
15.0	6.6	5.8

Cont…

Intensity of light ($mWcm^{-2}$)	Yield x 10^2 g	
	W-Lamp	Hg-Lamp
16.0	7.2	6.0
17.0	7.2	6.0
18.0	7.2	6.0

Table 4(b) : Effect of light intensity

pH = 3.0

[SNP] = 4.36×10^{-3} M

[Malonic Acid] = 5.76×10^{-3} M

Intensity of Light ($mWcm^{-2}$)	Yield x 10^2 g
	Sunlight
20.0	3.0
40.0	4.0
60.0	4.8
80.0	5.7
100.0	6.5
120.0	7.3
140.0	8.1
160.0	9.0
180.0	9.0
200.0	9.0
220.0	9.0

The results given above indicate that the yield of product 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. for tungsten-lamp and Hg-lamp light sources, I = 16.0 $mWcm^{-2}$ and for sunlight, I = 160.0 $mWcm^{-2}$, no reasonable increase in the yield of product has been observed. On using higher intensities of each light, it appears as if it reaches a saturation point at a particular intensity.

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.

Analysis of the product

The photochemical reaction between sodium nitroprusside and malonic acid 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 residue was recrystallised with methanol giving green crystals of the product, which was analysed as follows :

(i) Elemental analysis

Element	Found (%)	Calculated (%)
Fe	15.90	15.81
C	23.43	23.72
H	0.52	0.56
N	15.88	15.81
Na	25.82	25.98

(ii) IR spectral studies

A comparison of the i. r. spectra of the sodium nitroprusside, malonic acid 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.

Dicarboxylic acid normally absorbs at around 1700 cm^{-1} or little bit lower[15]. It has been reported that uncoordinated carboxylic group in copper (II)–NTA shifts higher as compared to the coordinated one[16]. Malonic acid absorbs at 1682 cm^{-1}, which shifts to a lower value of 1628 cm^{-1}. It indicates that the carboxylic group of malonic acid is not free in the product, but it is coordinated to the central metal ion, iron.

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

$$Na_4[Fe(CN)_4\,(C_3H_2O_4)]$$

In this case, malonate ion behaves as a bidentate ligand. One malonate ion has 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 the photochemical ligand exchange reaction of sodium nitroprusside has been proposed as –

$$Na_2[Fe(CN)_5(NO)] \xrightarrow{h\nu} Na_2[Fe(CN)_5(NO)]^*$$

$$Na_2[Fe(CN)_5(NO)]^* + H_2O \xrightarrow{h\nu} Na_3[Fe(CN)_5(H_2O)] + NO^+$$

$$Na_3[Fe(CN)_5(H_2O)] + C_3H_2O_4^{2-} \xrightarrow{h\nu} Na_4[Fe(CN)_4(C_3H_2O_4)] + H_2O + CN^-$$

Initially, the sodium nitroprusside is excited by absorbing incident radiations of a desired wavelength. Its excited state will then react with water and as a result, water enters the coordination sphere of iron, replacing nitrosylium ion (NO^+). This exchange in energetically favourable, because a neutral ligand like water (H_2O), can easily replace a cationic ligand (NO^+). Now, malonate ion can easily throw water molecule out of the coordination sphere of iron as anionic ligand can replace a neutral ligand. But, sidewise a cyanide ion will also be pushed outside the coordination sphere of iron as malonate is a bidentate ligand and it can enter the coordination sphere by replacing two monodentate ligands, i. e. water and cyanide ion. The replacement of cyanide ion is evident from the chemical analysis of the product as well as the usual positive response towards spot test for cyanide ion in the solution.

REFERENCES

1. J. H. Swinehast, Coord. Chem. Revs., **2**, 385 (1967).
2. R. P. Mitra, C. V. S. Jain, A. K. Banerjee and K. V. R. Chari, J. Inorg. Nucl. Chem., **25**, 1263 (1963).
3. B. B. Lal, Proc. Indian Acad. Sci., **A-14**, 652 (1941).
4. J. D. W. Van Voorst and P. Hemmerich, J. Chem. Phys., **45**, 3914 (1966).
5. W. Adamson and A. H. Sporer, J. Amer. Chem. Soc., **80**, 3865 (1958).
6. J. H. Swinehart and P. A. Rock, Inorg. Chem., **5**, 573 (1966).

7. P. A. Stoeri and D. X. West, J. Inorg. Nucl. Chem., **36**, 3883 (1974).
8. J. A. Mecleverty, Chem. Revs., **79**, 53 (1979).
9. S. Sahasi, Ph. D. Thesis, Sukhadia University, Udaipur, India (1991).
10. Q. H. Song and Q. Z. Lin, J. Photochem. Photobiol., **114A**, 181 (1998).
11. L. A. Anisimova, I. A. Yushenko and Toropova, J. Anal. Chem., **52**, 1049 (1997).
12. R. A. Baue and F. Basolo, J. Amer. Chem. Soc., **90**, 2437 (1983).
13. B. Durham, J. L. Walsh, C. L. Carter and T. J. Meyer, Inorg. Chem., **19**, 860 (1980).
14. Piyush J. Vyas, Ph. D. Thesis, Sukhadia University, Udaipur, India (2000).
15. C. Duval and C. Wadier, Anal. Chem. Acta., **23**, 541 (1960).
16. A. K. Bansal, S. C. Ameta and M. M. Bokadia, Acta. Chim. Hung., **111**, 267 (1982).

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