

PHOTOCATALYTIC REACTIONS OF SODIUM NITROPRUSSIDE

Suresh C. Ameta*, Manju Bala, Jatinder Kaur,
and
Sapna Sahasi

*Department of Chemistry
University College of Science
Sukhadia University
Udaipur (Rajasthan) 313 001, India*

الخلاصة :

لقد تمَّ دراسة تفاعلات الحفّازات الضوئية لنيتروبروسيد الصوديوم في وجود الضوء ، وأكسيد شبه موصل . وقد أُستخدمت أكاسيد الزنك ، والتيتانيوم ، والقصدير ، والتنجستين كمحفّزات ضوئية . كما تم إستقصاء تأثير المتغيرات المختلفة مثل تركيز نيتروبروسيد الصوديوم ، ومقياس الحمضية (pH) ، وطبيعة وكمية أشباه الموصلات على معدّل تفاعل الحفّازات الضوئية ، وأدت النتائج إلى افتراض مبدئي لميكانيكية تفاعل الحفّازات الضوئية .

ABSTRACT

The photocatalytic reaction of sodium nitroprusside was studied in the presence of light and semiconductor oxide. Zinc oxide, titanium dioxide, stannic oxide, and tungstic oxide were used as photocatalysts. Effects of variation of different parameters like concentration of sodium nitroprusside, pH, nature and amount of semiconductors on the rate of photocatalytic reaction were studied. A tentative mechanism for the photocatalytic reaction has been proposed.

*To whom correspondence should be addressed.

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INTRODUCTION

In sodium nitroprusside $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$, the nitric oxide has been assumed to be coordinated as NO^+ with the iron; however, this ligand (NO) is not considered as an innocent ligand. This means that it may coordinate with the central metal ion as NO^+ , NO , and NO^- because of the low-lying partly filled π -orbitals [1]. In the presence of light, an aqueous solution of this complex undergoes a complex decomposition process [2]. On the other hand, Mitra *et al.* [3] reported the production of a weak acid, when an aqueous solution of nitroprusside was irradiated with UV light. The blue compound $[\text{Fe}(\text{CN})_5(\text{NCS})]^{3-}$ can also be produced by photolysis of nitroprusside ion in the presence of aqueous thiocyanate [4]. It has been reported that the exchange reaction between $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ and CN^- is photocatalyzed [5]. A careful survey of the literature reveals that the photocatalytic reactions of sodium nitroprusside in the presence of semiconducting oxide and light had not been studied and, therefore, the present work was undertaken.

EXPERIMENTAL

Sodium nitroprusside (Sds), zinc oxide (EM), titanium dioxide (Sds), stannic oxide (Wilson), and tungstic oxide (BDH) were used in the present work. The solution of nitroprusside was prepared in doubly distilled water. The photocatalytic reactions of sodium nitroprusside were studied in the presence of semiconducting oxide and light. For this purpose, 10 cm^3 of nitroprusside solution of definite concentration was taken in a small beaker. A small amount (0.25 g) of semiconductor powder was added to this solution. The reaction mixture was exposed to a 1000 W halogen lamp (model OKANO). The pH of the solution was measured by a pH meter (Systronics Model 324). It was noticed that semiconductors caused turbidity in the solution. Therefore, measurement of optical density was difficult and the results could be erroneous. So, the centrifugate (centrifuge machine, REMI-1258) was always used for making optical measurements. A UV spectrophotometer (Systronics Model 108) was used to determine the λ_{max} of substrate as well as to observe the kinetics of the photocatalytic reaction by measuring the absorbance (optical density) of the solution at different time intervals.

RESULTS AND DISCUSSION

The λ_{max} for blank solution was observed at 400 nm which decreases on exposure to light in presence as well as absence of semiconductor. A new band developed at $\lambda_{\text{max}} = 720 \text{ nm}$ and 785 nm in presence and absence of semiconductor, respectively. This indicates that two different products are formed under photochemical and photocatalytic conditions. The spectra are given in Figure 1. A typical run is given in Table 1. A plot was drawn between $\log(\text{OD})$ and time where a straight line was obtained (Figure 2). It indicates that this photocatalytic reaction followed first order kinetics. The pseudo-first order rate constant (k_1) was determined from this plot using the reaction:

$$k_1 = 2.303 \times \text{slope.} \quad (1)$$

The effect of variation of different parameters on the rate of the photocatalytic reaction was studied.

Effect of Sodium Nitroprusside Concentration

The experimental observations are reported in Table 2. It is clear from the data that the increase in

Table 1. A Typical Run.

Time (min)	Optical density (OD)	2 + log OD	pH
0	0.366	1.5636	2.00
10	0.428	1.6314	2.00
20	0.494	1.6937	2.00
30	0.581	1.7642	2.00
40	0.664	1.8222	1.95
50	0.787	1.8960	1.95
60	0.895	1.9518	1.95
70	1.102	2.0422	1.90
80	1.230	2.0899	1.90

$\text{SnO}_2 = 0.25 \text{ g}$

[Sodium Nitroprusside] = $4.0 \times 10^{-2} \text{ M}$

$\lambda_{\text{max}} = 720 \text{ nm}$

Intensity = 80.0 mW cm^{-2}

Temperature = 303 K

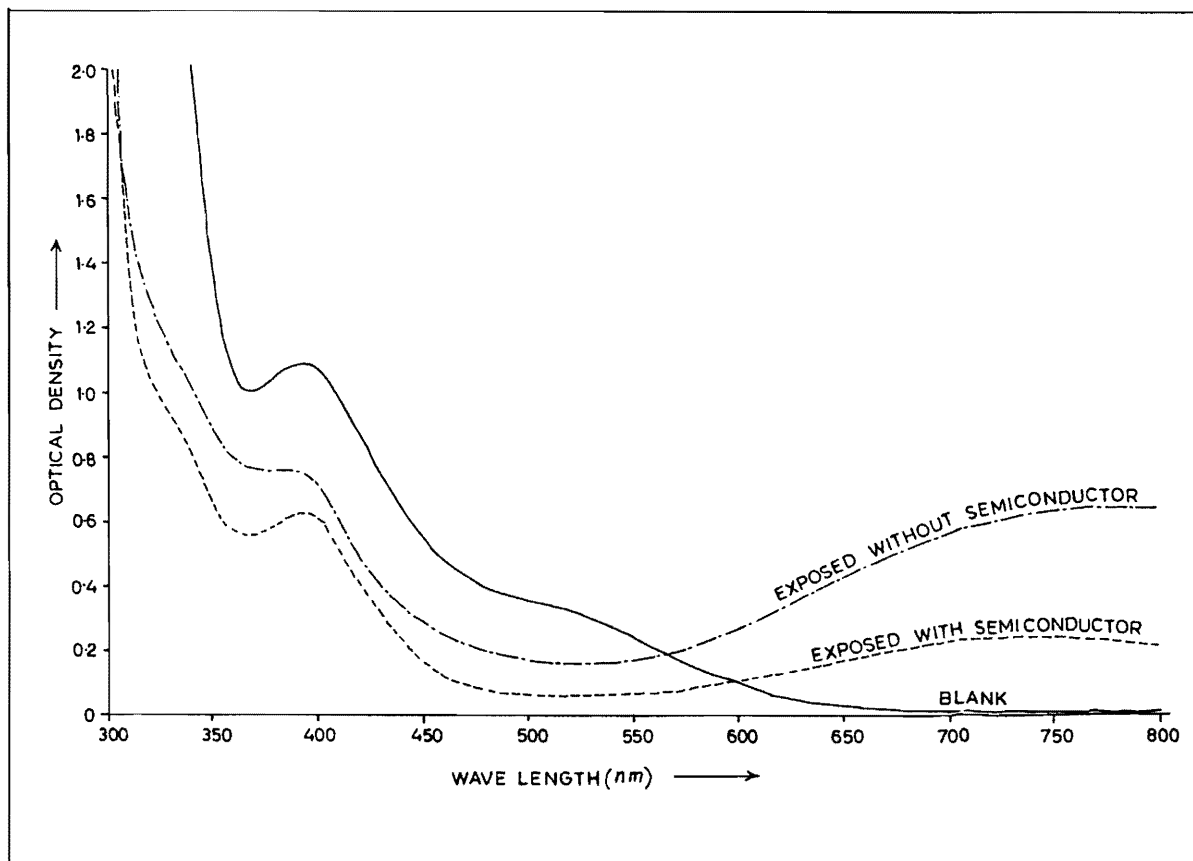


Figure 1.

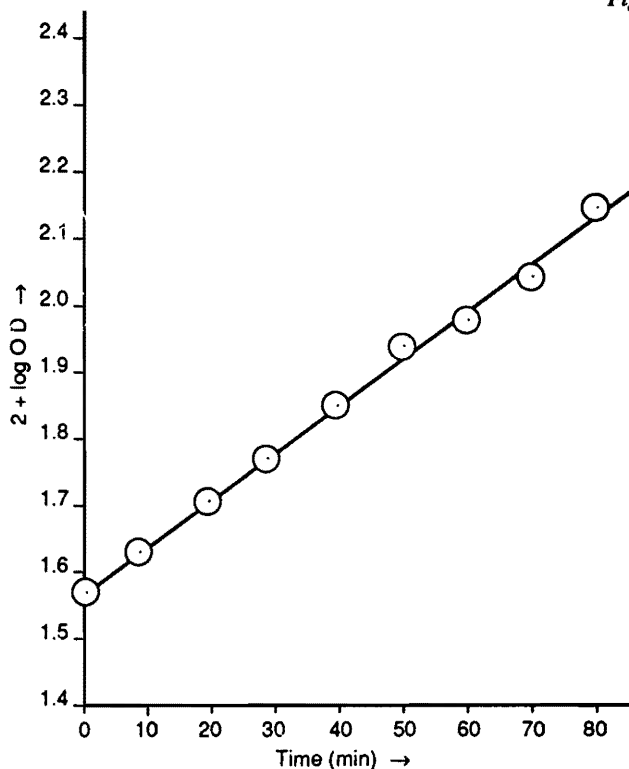


Figure 2. A Typical Run.

Table 2. Effect of Sodium Nitroprusside Concentration.

Intensity = 80.0 mW cm ⁻²		Temperature = 303 K
SnO ₂ = 0.25 g		
[Sodium Nitroprusside] × 10 ² M	k ₁ × 10 ² (min ⁻¹)	pH
1.5	0.97	1.85
2.0	1.02	1.85
2.5	1.08	1.90
3.0	1.15	1.90
3.5	1.27	1.95
4.0	1.40	2.00
4.5	1.31	2.00
5.0	1.18	1.95
5.5	1.13	1.90
6.0	1.04	1.90
6.5	0.98	1.90
7.0	0.92	1.85

the concentration increases the rate of photocatalytic reaction initially. Then the rate of the reaction attained a maximum value at [Sodium Nitroprusside] = 0.04 M. A further increase in the concentration resulted in a decrease in the rate of reaction. This may be explained on the basis that after an optimum concentration, any further increase in the concentration will act as a filter for light to such an extent that the desired intensity of the light will not reach to the semiconductor particles. This will cause a corresponding decrease in the rate of reaction.

Effect of pH

The rate of photocatalytic reaction of sodium nitroprusside was also studied at different pH values and the results are shown in Table 3. The rate of photocatalytic reaction was maximum at pH 2.0. Below this pH value, the relative concentration of H^+ ions increases which may decrease the rate of photosubstitution of NO^+ by H_2O , whereas, above this pH value, the relative concentration of H^+ ions will decrease. This decrease may facilitate the photosubstitution of OH^- ions along with the photosubstitution of H_2O to form hydroxo complexes, and, therefore, the rate of formation of $[Fe(CN)_5H_2O]^{3-}$ is likely to decrease.

Effect of Nature of Semiconductors

The rate of photocatalytic reaction of sodium nitroprusside was also studied in the presence of different semiconducting oxides (Table 4). These results indicate that in presence of different semiconductors, the rate of photocatalytic reaction of sodium nitroprusside is different. This may be due to their different band gaps (energy gap between valence and conduction bands). The order of their efficiency is $SnO_2 > WO_3 > TiO_2 > ZnO$.

However, this order does not follow the trend of their band gaps. It was observed that when ZnO was used, it turns grey towards the end of the reaction. In the case of zinc oxide, the blackening of semiconductor powder can be explained on the basis of these reactions:

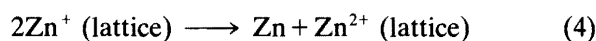
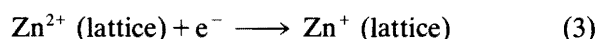
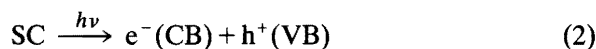


Table 3. Effect of Variation of pH.

[Sodium Nitroprusside] = 4.0×10^{-2} M SnO ₂ = 0.25 g Intensity = 80.0 mW cm ⁻² Temperature = 303 K	
pH	$k_1 \times 10^2$ (min ⁻¹)
1.0	0.51
1.2	0.63
1.4	0.69
1.6	0.77
1.8	0.96
2.0	1.40
2.2	0.86
2.4	0.69
2.6	0.57

Table 4. Effect of Nature of Semiconductor.

[Sodium Nitroprusside] = 4.0×10^{-2} M pH = 2.0 Intensity = 80.0 mW cm ⁻² Temperature = 303 K			
Semiconductor	Band Gap (eV)	λ_{\max} (nm)	$k_1 \times 10^2$ (min ⁻¹)
WO ₃	2.2	564	1.10
TiO ₂	3.1	400	0.98
ZnO	3.2	388	0.09
SnO ₂	3.5	354	1.40

Effect of Amount of Semiconductor

The dependence of the rate of photocatalytic reaction on the amount of semiconductors was also investigated (Table 5). It is clear from the above that the increase in the amount of semiconductor increases the rate of the photocatalytic reaction upto a certain amount of semiconductor. Further increase in the amount of the semiconductor do not cause any significant increase in the rate of the reaction, rather the rate of reaction remains almost constant. It shows that a saturation point is attained by the reaction with respect to increase in the amount of semiconductor.

This can be explained on the basis that with the increase in amount of the semiconductor, the surface area of the semiconductor will also increase; hence,

Table 5. Effect of Amount of Semiconductor.[Sodium Nitroprusside] = 4.0×10^{-2} M

pH = 2.0

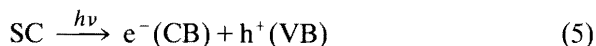
Intensity = 80.0 mW cm^{-2}

Temperature = 303 K

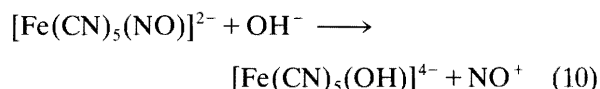
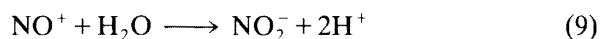
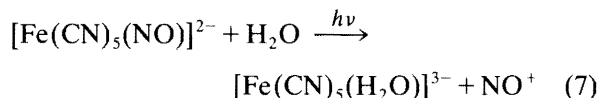
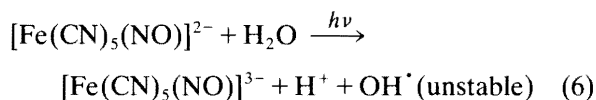
Amount of SnO ₂ (g)	$k_1 \times 10^2$ (min ⁻¹)
0.10	0.76
0.15	0.92
0.20	1.29
0.25	1.40
0.30	1.40
0.35	1.89
0.40	1.40
0.45	1.41
0.50	1.40

the rise in the rate of reaction. But after a certain limiting amount of the semiconductor, if the amount is further increased, then it will not contribute to an increase in the surface area. On the contrary, it will only increase the thickness of the layer of semiconductor powder at the bottom of the reaction vessel and thus the saturation point is reached. This has been also confirmed by employing reaction vessels of different dimensions. It was observed that in case of smaller reaction vessels, the saturation point was obtained earlier as compared to the vessels of larger dimensions, where it was obtained slightly later. This conclusion is further substantiated by the fact that this saturation point is shifted to a larger value on stirring the reaction mixture, which permits the exposure of all semiconductor particles.

On the basis of these observations, the following tentative mechanism for photocatalytic reaction of sodium nitroprusside may be proposed:



(semiconductor) (conduction band) (Valence band)



Initially, the corresponding ferric complex of sodium nitroprusside is formed, giving H^+ and $\cdot\text{OH}$ radicals. This complex is unstable and thus degrades. The substitution of NO^+ by H_2O in step (6) was investigated in the present investigations, which is a photocatalyzed as well as a photochemical reaction.

The electrons in the conduction bands of semiconductors are utilized in the Equation (7) to generate hydroxyl ions. This reaction will not contribute in solutions having $\text{pH} \leq 2.0$, but as the pH is increased, this may contribute to divert the reaction slightly to give a hydroxo-complex of iron. The generation of nitrite ions in Equation (9) was also confirmed by the usual test with starch-iodide paper.

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