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COPPER FERROCYANIDE PHOTOSENSITIZED OXIDATION OF DIPHENYLAMINE

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ABSTRACT

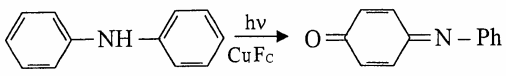
Photosensitized oxidation of diphenylamine was studied using copper ferrocyanide as sensitizer. Photosensitized oxidation products were separated by thin layer, column and gas chromatographic techniques. N – Phenyl – p – benzoquinonimine was identified as reaction product.

INTRODUCTION

It is believed that photocatalytic activity by inorganic minerals could have been very pronounced on primitive earth. Some inorganic substances that are component of earth crust possess photosensitizing activity and play the role of primary photosensitizers. It is surprising that the oxides of titanium, zinc and tungsten possess high photosensitizing activity in redox reactions comparable with the activity of porphyrines and chlorophylls. These compounds are able to sensitize reactions accompanied by light energy storage in terminal stable products. Recent investigations suggested that metal ferrocyanides of the form M_2 [Fe (CN) $_6$] .x H_2O, where M = Fe, Zn, Cu and Sn etc., might have abundantly existed on primitive earth environment. Metal ferrocyanides have acted as adsorbents [1–4] and ion exchangers [5–8]. Since many pi-conjugated compounds have excellent characters, various applications have been proposed [9]. Diphenylamine has several applications for examples, stabilizing nitrocellulose explosive and celluloid, spot tests, rubber antioxidant and accelerators, pesticides, pharmaceuticals, storage preservation of apples, industrial hair dryer, antioxidant and fungicide etc. [10–12]. Diphenylamine also have significant role in biological systems and some other biomedical applications [13-23]. Therefore work on photosensitized oxidation of diphenylamine seems to be very interesting. A search of literature indicated some report on oxidation [24-31] few report on photoreaction [32-36] and no report on photosensitized oxidation of diphenylamine. In view of this, attempts were made to study photosensitized oxidation of diphenylamine using metal ferrocyanide as sensitizer. In addition, present work describes photosensitized oxidation of diphenylamine (DPA) using copper ferrocyanide (CuFe) as sensitizer.

RESULTS AND DISCUSSION

In the present study irradiated solution of diphenylamine in the presence of copper feerocyanide on thin layer chromatographic separation give one additional spot in addition to spot of diphenylamine. Separation of product by neutral alumina column also indicated the formation of one reaction product. Eluent used was a mixture of petroleum ether and chloroform (80:20, v/v). The blackish blue and dark brown orange coloured bands were observed in the column. These coloured bands were collected in separate test tubes. The first band is column identified as DPA by gas chromatographic technique. Remaining band identified as n – phenyl – p – benzoquinonimine on comparing with synthesized authentic n – phenyl – p – benzoquinonimine by gas chromatographic technique. The schematic diagram for photosensitized oxidation of diphenylamine in the presence of copper ferrocyanide may be represented as :



The proposed reactions mechanisms for the photosensitized oxidation of diphenylamine in the presence of copper ferrocyanide may be outlined as follow:

$$\text{CuFe} \xrightarrow{h\upsilon} \text{CuFe}^* \quad (1)$$

$$\text{CuFe}^* + Ph_2NH \rightarrow Ph_2NH^* \text{ (or } Ph_2NH^{**}) + \text{Cu Fe} \quad (2)$$

$$Ph_2NH^* + Ph_2NH \rightarrow 2\ Ph_2NH + * \text{ (lower energy)} \quad (3)$$

$$Ph_2NH^* + O_2 \rightarrow \text{Product (PBQ) via further reaction} \quad (4)$$

Where CuFe and CuFe* are copper ferrocyanide in ground and lower energetic state, respectively; Ph_2NH, Ph_2NH^*, and Ph_2NH^{**} are ground, lower energetic and high energetic state of diphenylamine, respectively; O_2 is atmospheric oxygen. In the first step of reaction mechanism – I copper ferrocyanide reaches to lower energetic state in the presence of light . In the second step lower energetic copper ferrocyanied reaches to ground state via transferring its energy to diphenylamine molecule. In the third and fourth steps of reaction mechanism lower energetic diphenylamine either combined with another diphenylamine molecule with release of lower energy or reacted with atmospheric oxygen to form the product (PBQ) via further reaction. Photosensitized oxidation of diphenylamine is a catalytic process. The possible reaction mechanism - II for the above mentioned reaction may be one electron oxidation of diphenylamine by the photoexited copper ferrocyanide and subsequent reaction of the H_2O_2 (produced from following reaction of superoxide formed by reducation of copper) with the amine (or possible the amine cation radical).

EXPERIMENTAL SECTION

Chemicals

All chemicals used were of AnalaR grade and used as such without further purification. Copper(II) chloride ($CuCl_2.2H_2O$), potassium ferrocyanide, diphenylamine, sodium hypochlorite, and hydrogen peroxide were obtained from British Drug House (BDH, Poole, England). Silica gel – G and neutral alumina were obtained from Glaxo – laboratories, India.

Synthesis and Characterization of Copper Ferrocyanide

Copper ferrocyanide was synthesized similar to the method reported in chemical literature by Kourim's [37] by adding potassium ferrocyanide (167 ml; 0.1 M) solution slowly to copper(II) chloride (500 ml; 0.1 M) solution with constant stirring. Reaction mixture was heated on water bath at 100^0C for 2 – 3 h and then cured for 24 h. The precipitate was washed and dried at 60^0C. The final compound was grounded and sieved to (50 – 100) BSS mesh size. Copper ferrocyanide was characterized by elemental and spectral studies. Copper ferrocyanide is light reddish octahedral amorphous solid, has face centered cubic lattice [38] and show no X – ray pattern. Copper and iron were estimated by atomic absorption spectrophotometry on IL-751 spectrophotometer [39]. Carbon, hydrogen and nitrogen analysis was performed at Central Drug Research Institute, Lucknow, India on CEST-118, CHN Analyzer. Copper ferrocyanide was found to contain Cu, 28.30 %; Fe, 12.40 %; C, 16.03 %; H, 2.56 % and N, 18.32 % (calculated: Cu, 28.43 %; Fe, 12.49 %; C, 16.12 %; H, 2.68 % and N, 18.80 %) (yield 99.50 %) by elemental analysis. Copper ferrocyanide, $Cu_2[Fe(CN)_6].6H_20$, show a broad peak at around 3700 cm^{-1} characteristics of water molecule and OH group. Also a peak at 1600 cm^{-1} due to H-O-H bending. Two sharp bands at 2080 cm^{-1} and 580 cm^{-1} are characteristics of cyanide and Fe-C stretching, respectively. Another sharp band at 490 cm^{-1} probable shows the presence of copper - nitrogen band due to polymerization [40].

Characteristics of Diphenylamine

Diphenylamine (Physical state, white to yellow crystals; FW, 169.00; b.p., 302ºC; m.p., 53-54°C; density, 1.16; odor, floral; vapor density, 5.82; toxicity, oral rat LD 50: 200 mg/Kg) is slightly soluble in water and stable under ordinary conditions. Diphenylamine on inhalation irritates mucous membrane and contact with dust irritates eyes.

Synthesis of Authentic n-Phenyl-p-Benzoquinonimine

Authentic n-phenyl-p-benzoquinonimine (PBQ) was synthesized by adding dropwise freshly prepared cold sodium hypochlorite solution into diphenylamine (0.01 M, 100 ml) solution containing 10 ml of 30 % hydrogen peroxide with constant stiring. Orange brown coloured precipitate was obtained at room temperature 27 ± 1^0C. The orange brown coloured product was extracted with ether. During extraction procedure ether layer contained DPA and PBQ. The PBQ was separated from DPA and PBQ mixture by column chromatographic technique using neutral alumina (activated at 100^0C) column (packed in benzene) using benzene as eluent. PBQ has some role in biological systems and several biomedical applications [41-46].

Test on Oxidizing Capacity of Copper Ferrocyanide

Oxidizing capacity of copper ferrocyanide was tested by potassium iodide and starch solution. It was observed that test tube containing potassium iodide

solution (10 ml, 0.1 M), copper ferrocyanide (25 mg) and freshly prepared starch solution discharge blue colour of the reaction mixture.

Oxidation of Diphenylamine in Presence of Copper Ferrocyanide

Since copper ferrocyanide showed oxidizing behaviour toward potassium iodide solution. Diphenylamine have been testes for their oxidation in presence of copper ferrocyanide was added in the test tube containing 10 ml, 0.1 M solution of DPA. Slight change in the colour of diphenylamine solution and no change in absorption spectra were observed. So it was thought that diphenylamine solution is slightly oxidized due to copper ferrocyanide.

Irradiation of Reaction Mixture

A borosil test tube (14.5 x 2 cm) containing 20 ml, 0.1 M DPA solution and 0.5 gram of CuFe was irradiated for 6-8 h with 125 watt low pressure Hg-vapour lamp. Hg-vapour lamp was kept vertically above the test tube at a distance of 15 cm. It was found that DPA solution changed its colour and new peak appeared in absorption spectra. Exposure to the light on the solutions of above compounds in absence of CuFe showed very little oxidation. It appears that DPA solution could be photo – oxidized by CuFe. A study of the CuFe photosensitized oxidation of DPA has been done.

Separation and Identification of Products

Photo-oxidation products were separated by thin layer chromatographic (TLC) technique using silica gel as adsorbent and (TLC) plates were run into petroleum ether and chloroform mixture (80:20, v/v). A column of 45.0 cm height and 2.5 cm in diameter packed with neutral alumina was used for the separation of products. The fractions collected from column were identified by gas chromatograph.

CONCLUDING REMARKS

The use of copper ferrocyanide as sensitizer is a new finding therefore, it may be concluded from above studies that copper ferrocyanide can be used as a sensitizer in photo-oxidation of simple organic compounds. It may also be concluded from above studies that copper ferrocyanide have acted as possible photosensitizer during the course of chemical evolution on the primitive earth. The use of copper ferrocyanide as photosensitizer is more economical, therefore it has significant advantages over the use of other strong photosensitizers like titanium, zinc and tungsten oxides.

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