Asian Journal of Chemistry Vol. 12, No. 1 (2000), 299–301

Sensitized Photo-oxidation of L-Dopa

PRABHA MEHTA* AND S.C. MEHTA†
Department of Chemistry
K.R.G. Government Autonomons College
Gwalior-474 009, India

Photo-oxidation of L-Dopa was carried out by singlet molecular oxygen. Eosin yellow, rose bengal and methylene blue were used as dye sensitizers. After completion of reaction the products were isolated and characterised as carbon dioxide and dopamine by m.p., elemental analysis and spectral methods. The photo-oxidation was also carried out in the presence of singlet oxygen scavenger.

Levodopa is the single most effective drug in parkinsonism. It is used to elevate brain dopamine levels in patients with parkinsonism. Dopamine itself does not cross the blood brain barrier in sufficient concentration after systemic administration to be useful clinically. Since levodopa is an amino acid, it is accumulated in the brain by amino acid transport systems. In the presence of L-aromatic amino acid decarboxylase, levodopa is converted to dopamine[1].

In view of the biological importance of L-Dopa, dye sensitized photo-oxidation of levodopa was studied.

Photo-oxidation of L-Dopa has been carried out using eosin yellow as dye sensitizer. The photo-oxidation was also carried out in the presence of singlet oxygen scavenger nickel chloride. L-Dopa (2 g) was dissolved in conductivity water and taken in a reaction flask. To this eosin yellow (2 mL/4.50×10^{-3} M) was added. The solution was then irradiated keeping a distance of 20 cm between tungsten lamp and lower surface of the reaction flask. Oxygen was continuously bubbled through the solution with the help of oxygen cylinder. The progress of the reaction was observed after every twenty minutes by TLC. No solid product was separated from the solution during the reaction. After 32 h of irradiation new spot was observed on TLC. Reaction product was separated by preparative TLC. Solvent system used for TLC and preparative TLC was methanol : ethanol : conc. HCl : H_2O (8.3 : 4.2 : 1 : 3.1 v/v). Same experiment was repeated with methylene blue and rose bengal dyes.

Melting point was determined in sulphuric acid bath in open capillaries. IR and NMR of the reaction products were also recorded.

Photo-oxidation of L-Dopa gave two products (A) and (B). The gas evolved during irradiation was found to be carbon dioxide. Oxygen free from CO_2 is first passed through $Ca(OH)_2$ solution and then the outlet gaseous matter of the

---

†Department of Pharmacology, G.R. Medical College, Gwalior, India.

reaction mixture into same solution. The $Ca(OH)_2$ solution showed milkiness. Thus product (A) was identified as CO_2.

The second product (B) was recrystallised by CH_3OH. Its m.p. was found to be 287°C. The yield of product (B) was determined in the presence of eosin yellow, methylene blue and rose bengal and reported in Table-1.

TABLE-1
EFFECT OF SENSITIZERS ON THE YIELD OF PHOTO PRODUCT

S. No.	Dye used	Time of reaction (h)	Approx % of the yield of product B
1.	Eosin yellow	32	18
2.	Methylene blue	34	22
3.	Rose bengal	35	22

Participation of singlet oxygen was confirmed by using nickel chloride as singlet oxygen scavenger in the reaction mixture; the yield of product (B) was considerably reduced in the presence of scavenger. The results are summarised in Table-2:

TABLE-2
EFFECT OF SINGLET OXYGEN SCAVENGER

Dye sensitizer	Scavenger used	Time of reaction (h)	Yield of product (B) (%)
Eosin yellow	Nickel chloride	38	14
Methylene blue	Nickel chloride	40	16
Rose bengal	Nickel chloride	42	17

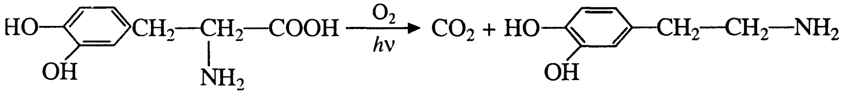
On the basis of elemental analysis, Found (%): C = 62.53, H = 7.99, O = 22.77, N = 10; $C_8H_{12}O_2N$ required (%): C = 62.33, H = 7.79, O = 20.76, N = 9.09.

Its infrared spectrum showed bands at 3042.65–3346.46 cm^{-1} which are due to phenolic hydroxy and amino groups. Bands at 1114.99–1614.13 cm^{-1} are due to OH and NH_2 groups (bending); bands at 935.82 cm^{-1} are due to tri-substitution of benzene (1,2,4-trisubstituted benzene).

Bands at 1449.95 and 1614.13 cm^{-1} may be due to C=C in plane vibration bands at 876.00 cm^{-1} are due to adjacent free hydrogen atom in benzene.

NMR peak at 6.8 ppm is due to aromatic proton. Peak at 6.6 ppm is due to —OH group corresponding to two phenolic —OH groups; peak at 3 ppm may be due to $—NH_2$ group; peak at 2.8 ppm is due to $—CH_2—NH_2$ protons.

On the basis of above analytical and spectral data the compound was identified as dopamine. Following tentative mechanism was proposed for the photo-oxidation of L-Dopa.



L-Dope (A) (B) Dopamine

These findings are in agreement with the work of Westhead[2] and Kim[3] who had suggested that in tyrosine photodynamic uptake of oxygen takes place with production of carbon dioxide along with two unidentified products.

ACKNOWLEDGEMENT

Authors are thankful to University Grants Commission (UGC), Bhopal for financial support.

REFERENCES

1. C.R. Craig and R.E Stitzel, Modern Pharmacology, Little Brown and Company, Boston, 4th Edn., p. 426 (1994).
2. E.W. Westhead, *Biochemistry*, **4**, 2139 (1965).
3. J.H. Kim, Univ. Microfilm, No. 65–12, 292 (1965).

(*Received*: 9 July 1999; *Accepted*: 21 October 1999) AJC-1894