

PHOTO-OXIDATION OF L(+) ASPARTIC ACID BY URANYL IONS

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The uranyl sensitized photodecomposition of L(+) aspartic acid has been carried out in acidic medium. Malonic acid has been characterised as the product of photo-oxidation of L(+) aspartic acid and a tentative mechanism for the photo-oxidation has been proposed.

Key words: Oxidation of amino acids, uranyl ions aldehyde formation by hydrolysis.

INTRODUCTION

A critical survey of the literature reveals that a great deal of work on the oxidation of amino acids by different oxidants has been carried out by many workers [1-8], but the photo-oxidation of amino acids by uranyl ions has so far received negligible attention [9-12]. Therefore, the photo-oxidation of L(+) aspartic acid by uranyl ions has been carried out in acidic medium and the results are reported in the present communication.

EXPERIMENTAL

Stock solution of L(+) aspartic acid (SD), uranyl sulphate (BDH) and sulphuric acid (SM 'GR') were prepared in doubly distilled water and a reaction mixture of the composition L(+) Aspartic acid: UO_2^{2+} : H_2SO_4 : H_2O = 15:5:1:29 v/v was prepared in a dark coloured bottle. Concentrations of the reactants in reaction mixture were;

$$\begin{aligned} [\text{L}(+) \text{ Aspartic acid}] &= 1.5 \times 10^{-2} \text{ M} \\ [\text{UO}_2^{2+}] &= 1.0 \times 10^{-3} \text{ M} \\ [\text{H}_2\text{SO}_4] &= 0.1 \text{ M} \end{aligned}$$

The reaction mixture was exposed to a 200 W (Sylvania) tungsten lamp kept at a distance of 30 cm, a water cell being used as the infrared filter. The progress of the reaction was studied by the thin layer chromatographic method at different time intervals, using *n*-butanol: acetic acid: water (12:3:5) as the solvent system. In the initial stage a single spot corresponding to L(+) aspartic acid ($R_f = 0.42$) was observed when the TLC plate was placed in iodine chamber.

As the reaction proceeds, a new spot ($R_f = 0.60$) was also detected along with a spot of unreacted aspartic acid. It indicated that some product has been formed. A slight turbidity was observed and the residue filtered corresponded to the same product (Co-TLC).

RESULTS AND DISCUSSION

The product was separated by the preparative T.L.C. method, dissolved in water and recrystallized.

This solid melts at 135° and gave the characteristic test for malonic acid [13]. It was further confirmed by following the spectral data.

u.v. λ_{max}	207 nm. due to the presence of carboxylic group.
KBR	
i.r. ν_{max}	2855, 1358 cm^{-1} are due to simple C-H stretching and bending vibrations. 1702, 1700 cm^{-1} are due to saturated aliphatic carboxylic groups.
n.m.r. 7.25	(singlet) indicates the presence of methylene ($-\text{CH}_2-$) group.
- 1.95 τ	(s) represents a carboxylic proton.
Mass $m/e = 104$	(0.25%) indicating the molecular weight of the product.
$m/e = 77$	(1.4%) indicates the loss of carbon monoxide molecule (decarbonylation).
$m/e = 45$	(100%) is due to $[\text{M} - \text{CH}_2\text{COOH}]^+$
$m/e = 59$	(0.42%) is due to loss of carboxylic group from the parent ion.
$m/e = 60$	(86-90%) may be observed by the loss of carbon dioxide molecule from the parent ion.
$m/e = 43$	(96.22%) is due to the acetyl ion.

On the basis of the chemical and spectral data the product was confirmed as malonic acid.

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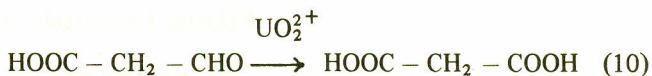
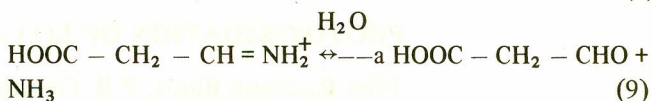
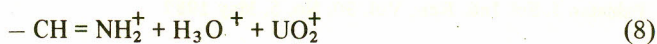
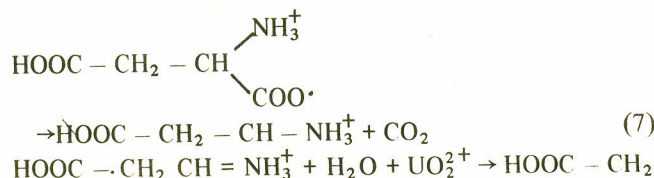
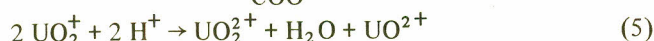
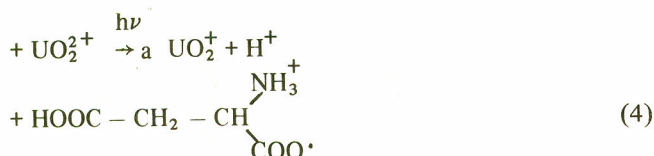
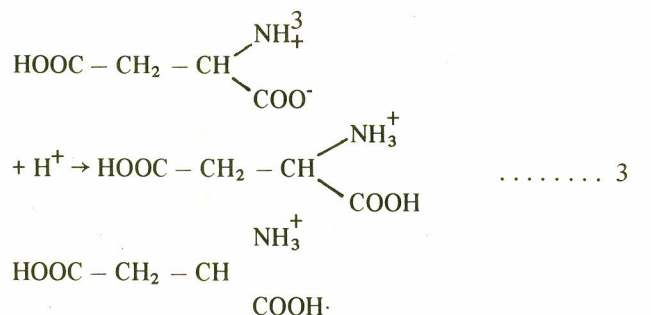
It was observed that the yield of the product increases on passing oxygen in the reaction mixture during the period of irradiation. Some control experiments were carried out in the absence of uranyl salt, light and oxygen. It was found that the reaction does not proceed in the absence of first two and, therefore, it can be concluded that the presence of uranyl salt and light is necessary for the oxidation of aspartic acid. It was observed that the yield of the photo-product increases by about 20-30 % on passing oxygen in the reaction mixture. The increase in yield may be due to the regeneration of U(VI) from U(IV) [14] and the acid present will assist in the production of U(VI) from U(V) [15] resulting in increase in the yield.



The reaction was also carried out in the presence of acrylamide where the formation of viscous mass (through polymerization of acrylamide) indicates the formation of free radicals in the reaction path.

The presence of carbon dioxide and ammonia (as ammonium ions) was also detected by their usual tests with lime water and Nessler's reagent.

On the basis of these observations a tentative mechanism for the photo-oxidation of L(+) aspartic acid by uranyl ions may be represented as follows:



The formation of protonated imine in reaction [8] and its hydrolysis to corresponding aldehyde is in confirmation with the mechanism proposed earlier for the oxidation of amino acids [7, 8, 16, 17]. The aldehydes have been reported as the reaction products of oxidation of different amino acids by various workers [1, 3, 7, 8, 18, 19]. In the present work also, the aldehyde is formed by hydrolysis of protonated imine in reaction [9]. It is further oxidised to malonic acid by uranyl ions as reported in the case of formaldehyde and acetaldehyde by earlier workers [20, 21]. However, the oxidation of malonaldehyde to malonic acid may also be due to oxygen.

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REFERENCES

1. M.Z. Barkat, M.F.A. Wahab and M.M. Elsadar, J. Chem. Soc., 4685 (1956).
2. O.G. Pokrovskaya, Izvest. Sibir. Otd. Akad. Nauk SSSR, 8, 50 (1959).
3. R.S. Verma, J.M. Reddy and V.R. Shastri, J. Chem. Soc. Perkin II, 469 (1976).
4. J.K. Sthapak and S. Ghosh, J. Indian Chem. Soc., 47, 347 (1970).
5. W.U. Malik, R. Bemb, M.P. Teotia and R.N. Goyal, J. Indian Chem. Soc., 53, 605 (1975).
6. M. Adinarayan, B. Sethuram and T. Navneethrao, J. Indian Chem. Soc., 52, 877 (1976).
7. S.C. Ameta, P.N. Pande, H.L. Gupta and H.C. Chowdhry, Acta, Chim., 110, 7 (1982).
8. C. Neuberger, Biochem. Z., 13, 683 (1908).
9. R. Bhatt, P.B. Gandhi, S.C. Ameta and H.C. Chowdhry, Bull. Soc. Chim. Belges (communicated).
10. R. Bhatt, P.S. Shrimali, S.C. Ameta and H.C. Chowdhry, Z. Phys. Chem. (Leipzig) 267, 817 (1986).
11. R. Bhatt, P.S. Shrimali, S.C. Ameta and H.C. Chowdhry, Accepted for presentation at the XI IUPAC Symposium on Photochemistry Lisbon (Portugal),

27 July 1 Aug. '86.

13. H. Singh, G. Saxena and A. Kumar, *Advanced Practical Chemistry*, (Mira Prakashan, Agra (India), 1980), Vol. II. 3rd ed. p. 41.
14. V.N. Ushataskii and Y.M. Tolmachev, *Trudy Radiovogo Inst. im. V.G. Kholpina, Khim. i. Geokhim Z.*, 98 (1956).
15. D.H. Volman and J.R. Seed, *J. Am. Chem. Soc.*, **86**, 5095 (1964).
16. S.C. Ameta, P.N. Pande, H.L. Gupta and H.C. Chowdhry, *Ciencia E. Cultural*, **34**, 1419 (1982).
17. S.C. Ameta, P.N. Pande, H.L. Gupta and H.C. Chowdhry, *Ciencia E. Cultura*, **35**, 1885 (1983).
18. K. Kumar and L.K. Saxena, *J. Indian Chem. Soc.*, **47**, 435 (1970).
19. Govind Chandra and S.N. Shrivastava, *Indian J. Chem.*, **11**, 773 (1973).
20. K. Venkatrao and M. Santappa, *Current Sci., India*, **33**, 709 (1964).
21. K. Venkatrao and M. Santappa, *Z. Physik. Chem. Frankfurt*, **54**, 101 (1967).

Most of the chemical properties of pond bottom soil were inversely correlated with exchangeable Na of adjacent land soil in case of Grey and NCDGF soil types. Again, the exchangeable Na of land soil had strongly ($r > 0.001$) inverse effect on the fluctuations of pH ($r = -0.744$), total N ($r = -0.696$), exchangeable K ($r = -0.757$), exchangeable Na ($r = -0.680$) and direct effect on the fluctuation of exchangeable N ($r = 0.897$) in the case of NCDGF soil. The total N of land soil directly and inversely influenced the fluctuations of all chemical properties of pond bottom soil in the case of NCDGF, CDGF and CBF soil units respectively in the case of intracorelations in the chemical properties of pond bottom and adjacent land soil only exchangeable Na had maximum inverse correlations with other chemical properties in three soil types.

Key words: Soil units; Pond bottom soil; Adjacent land soil.

were collected with a spade. The samples were dried in the room, ground and sieved by a 0.3 mm sieve and kept in plastic packets with labels for chemical analyses.

All the samples were analysed for pH, total N, available P, exchangeable K, Ca and Na. Soil pH was determined in soil-water suspension of 1:2.5 and total N by Macro-Kjeldahl method [7]. Available P was extracted with 0.5 M NaHCO_3 and was analysed colorimetrically by ascorbic acid reduction method [8]. Exchangeable K, Ca and Na were analysed from ammonium acetate extract by Eppendorf Flame Photometer [9].

The three soil types in relation to USDA soil taxonomy and FAO/UNESCO Legend according to Brunner [10] are as follows:

General soil type	USDA soil taxonomy	FAO/UNESCO Legend
1. Grey Flood-plain (GF)	Mainly Haplic gypsis	Eutric Fluvisols
2. Noncalcareous Floodplain (NCDGF)	Haplic gypsis	Eutric Fluvisols
3. Calcareous Floodplain (CDGF)	Haplic gypsis and Eutrochrepts	Calcaric Fluvisols and Calcaric Cambisols

INTRODUCTION

In ponds, the nutrient status of water almost wholly depends upon the pond bottom soil. Both inorganic and organic nutrients enter the pond with land washes from adjacent land, and dead aquatic plants and animals. These settle in the bottom soil which releases nutrients by bacterial decomposition through biogeochemical cycle [1-3].

The primary producer, i.e., phytoplankton, grows and ultimately influence the growth of fish as food. Land-pond bottom soil and soil water interactions play a vital role in the growth and abundance of aquatic life. Therefore, the fertility and nutrient status of pond soil and water partially depend upon the adjacent land soil. Again, the results on the interaction and correlation between the nutrients of both pond bottom and adjacent land soil is very rare but very essential to know. Little work has been done on soil nutrient status of land of various soil units [4-6]. The present work therefore has been undertaken to study the inter and intra correlations among some chemical properties of pond bottom and its adjacent land soil of three Bangladeshi soils.

MATERIAL AND METHODS

Soil samples were collected from three soil types, such as GF (Eutric Fluvisols), NCDGF (Eutric Fluvisols) and CDGF and CBF (Calcaric Fluvisols and Calcaric Cambisols) soils. Pond bottom samples were collected with the help of Ekman Dredge and land soil samples of 0-13 cm depth