

UV – INDUCED SYNTHESIS OF AMINO ACIDS FROM AQUEOUS STERILIZED SOLUTION OF AMMONIUM FORMATE AND AMMONIA UNDER HETEROGENEOUS CONDITIONS

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ABSTRACT: Irradiation of sterilized aqueous solution of ammonium formate and ammonia with UV light in the presence and or absence of certain inorganic sensitizers for 25 hrs. gave six ninhydrin positive products in appreciable amounts. Out of the six products observed five were characterized as lysine, serine, glutamic acid, n-amino butyric acid and leucine. The sensitizing effect of additives on ammonium formate was observed in the order; uranium oxide > ammonium formate > ferric oxide > arsenic oxide.

INTRODUCTION

The abiotic synthesis of specific life forming molecules has been discussed by Oparin, Haldane, Oro, Ponnampertuma and others¹⁻⁸. They have emphasized that the molecules that are fundamental today were fundamental at the time of abiogenesis of living matters. It has been suggested that in the ancient abiotic period of earth, diverse types of organic compounds would have been formed by various methods which would not have required any kind of living or vital forces. Ammonium formate, one of such compounds in presence of ammonia was irradiated by ultraviolet light with a view to see the formation of life forming molecules.

Formation of amino acids by thermal decomposition of ammonium formate (oligomerization of HCN) and the effect of X-Ray and glow discharge electrolysis of aqueous and ammoniacal solution of ammonium formate has been studied earlier³⁻⁶. However, the action UV light on aqueous solution of ammonium formate in presence of ammonia under heterogenous conditions has not yet been studied. Therefore, it was considered of interest and the effect of UV light on aqueous solution of ammonium formate and ammonia in the presence of different metal oxides has been studied and the results have been presented in this communication.

MATERIALS AND METHODS:

Extra pure ammonium formate (0.01 mole) was dissolved in 10% aqueous ammonia and redistilled water (pH 9.0 ± 0.5). 250 ml of this solution was taken in each of four sterilized quartz glass vessels. Extra pure inorganic sensitizers were then added to three vessels under aseptic conditions. The purity of sensitizers was tested prior to their addition to the experimental solutions. The flasks were kept under UV irradiation chamber for a period of 25 hrs. The exposed solutions were drawn out aseptically, concentrated in a rotatory vacuum evaporator, examined for any microbial contamination by usual techniques and then

the portions of the concentrates were analysed chromatographically employing Whatman No.1 paper (18.5 x 22.5", 24 hrs. at $20 \pm 2^\circ\text{C}$), Silica Gel G or cellulose layer (MN 300) as stationary phase and n – butanol; acetic acid; water (4;1;1, v|v; 9;1;1; v|v) or n – butanol; acetic acid; pyridine water (15;3;10;12, v|v) as solvent systems. The results were also confirmed by electrophoresis (pH 1.6, buffer, 90% formic acid; acetic acid; water, 40; 60; 1, 600 ev, 40 mA, 25 min). The authentic amino acids were run concurrently alongside of the concentrate as reference standards.

TABLE I

Results of UV Irradiation (25% HRS) of Ammonium Formate, Ammonia and Water under Heterogeneous Conditions.

Reaction Mixture	Products of Photochemical synthesis					
	I	II	III	IV	V	VI
AF + W + NH ₃	++	+	++	++	+++	++
AF + W + NH ₃ + UO ₃	+++	+	+++	+++	+++	+++
AF + W + NH ₃ + Fe ₂ O ₃	+	+	+	+++	++	T
AF + W + NH ₃ + As ₂ O ₃	-	++	-	+++	-	-
Rf (%) in	7.2	14.5	-	19.0	38.4	59.6
(i) BAW	36.4	43.8	-	50.4	67.4	74.8
(ii) BAPW-						
Colour with	V	V	V	V	V	V
ninhydrin	PV	BP	-	PB	P	RV
isatin	GBr	GBr	-	BGr	GrB	GBr
Folin's Reagent	R	R	-	R	OR	R

Alloxan	BW	BW	W	W	BV	BW
Fluorescence in UV black light lamp						
DNP Dvts.	-	33.1	-	-	49	58
*Rf (%)	Lys	Ser	-	Glu	Amino-n-Buty	Leu

‘-‘ not detected; ‘+’ positive test or poor yield; W – water or white; B – blue; R – red; V – violet; G – grayish; Gr – green; P – purple; D – dark; AF – ammonium formate; Lys – lysine; Ser – serine; Glu – glutamic acid; amino – n –buty n – amino – butyric

acid; Leu – leucine; BAW – (butanol: acetic acid; Water, 4:1:1, v|v) BAPW – (butanol: acetic acid: pyridine: water, 15:3: 10:12 v|v at $18 \pm 2^\circ\text{C}$, Rf – in test amyl alcohol: 3% ammonia (1:1, v|v)

The Chromatogram was first dried in air, then at 60°C , examined under UV black light lamp for marking fluorescent spots and eluted with water for further characterization. For locating and characterizing the resulting products ninhydrin (0.1 g | 100 ml acetone), alloxan (0.2 g | 100 ml acetone), isatin (0.2 g | 100 ml acetone) and Folin’s reagent (0.02% 1 – 2 naphthaquinone 4 – sulphonate in 5% aqueous sodium carbonate) were used as colour producing reagents DNP derivatives

of provisionally identified amino acids were prepared and characterized by comparing their properties with authentic DNP amino acids¹⁰⁻¹⁵. Thus the photolytic products were characterized DNP aminoacids, Rf value, m.p. mixed m.p. of DNP derivatives, coincidence chromatography, noting their characteristic fluorescence under UV black light lamp (365 nm) and also by specific chemical and spectral methods using Beckmann Spectrophotometer and Perkin Elmer 521 Spectrophotometer.

RESULTS AND DISCUSSION

When an aqueous solution of ammonium formate was exposed to UV light for 10 hrs. in presence of ammonia only two products appeared on the paper, (II & IV). Out of these, product II was formed in appreciable amount while product IV was formed in poor amount. Further irradiation upto 25 hrs. resulted in the formation of six products (I to VI). There was a marked decrease in the concentration of product II. Product V was formed in higher concentration as compared to other amino acids. When uranium oxide was used as a sensitizer the concentration of all photoproducts (I – VI)

increased. In presence of iron oxide product VI was formed in poor amount. When the reaction mixture of ammonium formate, ammonia and water was irradiated in presence of arsenic oxide the number of amino acids formed was retarded. Only two amino acids II & IV were detected. It was therefore observed that the sensitizing effect of different oxides used was in the order; Uranium Oxide, ferric oxide, arsenic oxide. Out of the six products formed, five products were characterized as lysine (I), serine (II), glutamic acid (IV), 2-amino-n-butylric acid (V), and leucine (VI).

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