

UV Induced Evolution of Amino Acids under Possible Primitive Conditions of the Earth

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Amino acids *viz.* lysine, aspartic acid, serine, glycine, glutamic acid, threonine, α -alanine, β -alanine, α -amino-butyric acid, valine, isoleucine and leucine were formed as a result of irradiation of aqueous sterilized solution of allyl alcohol and ammonia with UV light of wavelength 2537Å. The presence of oxides *viz.*, ZrO₂, TiO₂, colloidal Fe₂O₃, MnO₂ and colloidal MoO₃ exerted a marked effect on the nature and yield of the photo products.

INTRODUCTION

Abiotic synthesis of possible precursors of life forming molecules has been studied by a number of workers.¹⁻⁴ Formation of amino acids from intermediates *viz.*, saturated alcohols, aldehydes and acids⁵⁻⁹ is also reported. However, synthesis of amino acids from unsaturated alcohols has not received much attention. The present work attempts to investigate UV induced synthesis of amino acids from reaction mixtures of allyl alcohol-ammonia and water in the presence and absence of various oxides.

MATERIALS AND METHODS

Low pressure mercury vapour lamp (250 w) was used to provide UV light of wavelength 2537 Å. Quartz glass vessels of 300 mL capacity were placed in specially designed air cooled chamber at room temperature ($18 \pm 2^\circ\text{C}$). Prolonged time periods of irradiation upto 40 h were used. The mixtures in the present study were sterilized solutions of allyl alcohol in double distilled water (1/100 v/v) at pH ± 0.5 . Oxide sensitizers (5 mg/100 mL water or 0.5 mL/100 mL water) were tested for their purity prior to addition in the reaction system. Portions of irradiated solutions were taken out aseptically after 10, 20, 30 and 40 h exposure, concentrated in vacuum evaporation and analysed chromatographically on Whatman No. 1 paper both by uni- and two-dimensional chromatography¹⁰ using *n*-butanol-acetic acid-water (4 : 1 : 1 v/v) and *n*-butanol-acetic acidpyridine-water (15 : 3 : 10 : 12 v/v) as solvents.¹¹ Ninhydrin reagent¹² was used to locate amino acid spots on chromatogram. Further identification was made by colour tests with a variety of reagents *viz.*, isatin,¹³ Folin's reagent¹⁴ and alloxan;¹⁵ R_f value measurements and also by spectral methods.¹⁶ Products were eluted for chemical

tests by thin layer chromatography on silica gel G.¹⁷ Photochem calorimeter MKIII was used for quantitative determination of amino acids. UV absorption spectrum of irradiated mixture was recorded in aqueous medium in Beckman DK-2 spectrophotometer.

RESULTS AND DISCUSSION

Tables 1 and 2 show the results of irradiation of allyl alcohol-water-ammonia mixture for different periods of time up to 40 h. Eight chromatographically detectable and ninhydrin positive products are found in 10 h exposure. Three more ninhydrin positive products are added in further 10 h irradiation. After 30 h exposure, fourteen products were detected. Further increase of irradiation time up to 40 h shows marked decrease in product yields. Of the fourteen products so formed, twelve were identified as lysine (I), aspartic acid (II), serine (IV), glycine (V), glutamic acid (VI), threonine (VII), α -alanine (VIII), β -alanine (IX), α -amino butyric acid (XI), valine (XII), isoleucine (XIII) and leucine (XIV). Relatively good yield for products IV, V, VIII, IX, XI, XII and XIV is also seen in Table 1. Products II, V, VIII and XII were also confirmed by UV absorption spectroscopy (Fig. 1).

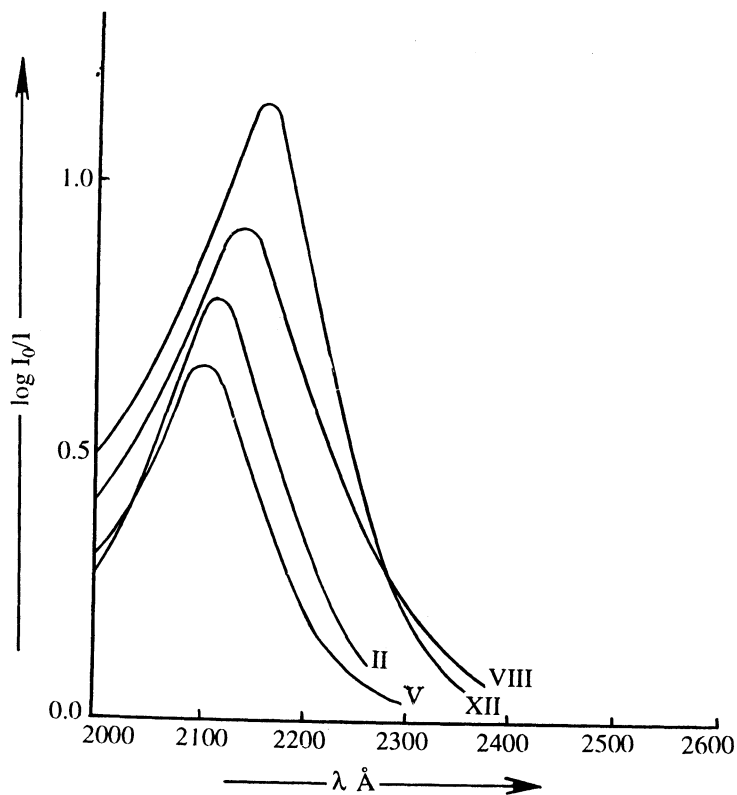


Fig. 1. UV absorption spectra of some photo products of irradiated aqueous solution of allyl alcohol and ammonia (30 h)

TABLE-1
EFFECT OF UV RADIATION ON AQUEOUS STERILIZED SOLUTION OF ALLYL ALCOHOL AND AMMONIA (pH 10 ± 0.5)

Composition of reaction mixture/ properties	Exposure period (h)	Products of irradiation													
		I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	XIII	XIV
allyl alcohol + ammonia + water	10	—	—	T	+	+	+	T	++	+	—	—	—	—	—
	20	—	T	+	++	++	+	+	+++	++	—	—	—	T	+
	30	++	++	+	+++	++++	+	++	++++	+++	++	++	++	++	+++
	40	+	+	+	++	+++	T	+	+++	++	+	+	—	T	++
R _f (%) in solvent systems	8.8	12.2	13.2	14.0	15.2	18.0	20.0	22.2	24.0	25.2	31.4	44.0	52.2	56.4	
(a) B.A.W.	38.0	40.0	42.4	43.0	44.0	50.0	52.0	54.0	56.1	58.0	62.4	64.6	67.8	74.0	
(b) B.A.P.W.															
Colour with															
(a) Ninhydrin	V	BV	V	V	RV	V	V	BV	V	V	V	V	V	V	
(b) Folin's reagent	GBr	Gr	G	GBr	GY	BG	G	G	G	G	G	G	G	GY	
(c) Isatin	BrP	dB	dB	P	BrP	PB	P	dB	dB	P	P	BrP	BrP	BP	
(d) Alloxan	RV	dR	R	R	R	R	OR	R	OR	R	OR	dR	dR	R	
Stability in															
(a) ether	ins	ins	ins	ins	ins	ins	ins	ins	ins	ins	ins	ins	ins	ins	
(b) water	s	s	s	s	s	s	s	s	s	s	s	s	s	s	
Amino acid identified	Lysine	Aspartic acid	—	Serine	Glycine	Glutamic acid	Threonine	α-alanine	β-alanine	α-amino acid	α-butyric acid	valine	iso-leucine	leucine	

V, violet; B, blue; R, red; Br, brown; P, purple; G, green; Gr, gray; Y, yellow; O, orange; d, dull; ins, insoluble; s, soluble; —, not detected/ unidentified; T, trace amount; +, low yield; ++, moderate yield; +++, good yield; +++++, high yield.

B.A.W., *n*-butanol : acetic acid : water as 4 : 1 : 1 vol/vol at 16 ± 2°C.

B.A.P.W., *n*-butanol : acetic acid : pyridine: water as 15 : 3 : 10 : 14 vol./vol. at 16 ± 2°C.

TABLE-2
 DETERMINATION ($\mu\text{g}/1000 \text{ mL}$) OF PRODUCTS FORMED BY UV IRRADIATION (30 h) OF ALLYL ALCOHOL-AMMONIA-WATER SYSTEMS
 ($\text{pH} = 10.0 \pm 0.5$) IN THE PRESENCE AND ABSENCE OF OXIDES

Reaction mixture with	Productions of irradiation													
	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	XIII	XIV
no oxide	0.002	0.006	0.003	0.056	0.048	0.005	0.028	0.126	0.140	0.035	0.062	0.061	0.048	0.072
ZnO ₂	T	T	0.001	0.002	0.003	T	0.001	0.020	—	T	—	—	T	—
TiO ₂	0.003	0.033	0.015	0.064	0.031	0.046	0.025	0.072	0.080	0.050	0.042	T	0.038	T
Colloidal Fe ₂ O ₃	0.002	0.036	0.033	0.076	0.048	0.042	0.050	0.080	0.084	0.073	0.040	T	0.022	T
MnO ₂	T	0.034	T	0.042	0.032	0.018	0.028	0.065	0.038	0.074	0.026	T	0.025	T
Colloidal MoO ₃	0.001	0.001	0.003	0.076	0.064	0.125	0.129	0.095	0.135	0.226	0.025	0.061	0.079	0.080

—, not detected; T, trace amount; coll., colloidal.

A marked effect was noticed on the photochemical synthesis of amino acids when identical solutions of allyl alcohol, ammonia and water were irradiated separately in the presence of oxides. Photochemical formation of amino acids was retarded when ZrO_2 was used as sensitizer. Products IX, XI, XII and XIV could not be detected and the other photo products showed faint presence only. Presence of TiO_2 in the reaction mixture gave all the fourteen products (Table 2). Of these serine (IV), α -alanine (VIII) and β -alanine (IX) were formed in appreciable amounts. Products glycine (V), glutamic acid (VI), α -amino butyric acid (XI) and isoleucine (XIII) were formed in moderate amounts whereas the others were formed in smaller amounts. In the presence of colloidal Fe_2O_3 , same photo products were formed in moderate amounts. Products XII and XIV were formed in traces. Presence of MnO_2 showed a moderate effect (Table 2). Highest yield of photo products was observed in the presence of colloidal MoO_3 .

Thus it may be inferred that allyl alcohol appeared as an intermediate during the photochemical evolution of amino acids under primitive earth conditions. The catalytic role of mineral oxides then present is also important.

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