Alanine Formation in Aqueous Solution of Ammonium Acrylate Induced by UV Picosecond Laser Pulses

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Formation of amino acids (α - and β -alanine) and oligomers containing NH_2 -groups, have been discovered under the irradiation of aqueous solution of ammonium acrylate by picosecond laser pulses with intensity up to 1 GW/cm^2 , $\lambda = 266 \text{ nm}$.

The composition of photoproducts was shown to depend on intensity of laser pulses. The laser intensity dependence of the β -alanine quantum yield was of a nonlinear character. The β -alanine formation occurred under the excitation of highly singlet electronic states of ammonium acrylate molecule by two quanta of UV or one quantum of VUV light. The unimolecular mechanism of amino acid formation in such a reaction was suggested.

KEY WORDS: Amino acids, photochemical synthesis, nonlinear photochemistry, picosecond laser pulses irradiation.

INTRODUCTION

The formation of amino acids under the action of ultraviolet radiation was investigated mainly in the course of laboratory simulation of abiogenous syntheses of simple biomolecules. The reactions in both gas phase and aqueous solutions were observed to include a chain of intermediate radical transformations which gave rise to a mixture of various photoproducts as well as amino acids with a small total quantum yield ($10^{-4} \div 10^{-5}$).¹⁻³

The use of a powerful laser source of UV radiation with its pulse duration of the order of a few picoseconds made it possible to synthesize amino acids in solutions of ammonium salts of α , β -unsaturated dicarboxylic acids by effecting the two-step excitation of the higher electronic states in the parent molecules.⁴ The process of nonlinear photochemical formation of amino acids was found to display some specific features:

- 1) an amino acid was the only photoproduct corresponding to the addition of ammonia to the C=C bond;
- 2) very high quantum yield of the amino acid;
- 3) the secondary products of radical reactions including those produced by the interaction with water⁵ were absent.

Consequently this made necessary the assumption that two-quantum excitation of the higher electronic states of the molecules would cause the unusual mechanisms of photochemical reactions.

In this connection, it was advisable to study under similar conditions the photochemical interaction of ammonia with a mono-basic α , β -unsaturated acid (unsymmetrical with respect to the C=C bond) which can, in principle, yield α - and β -amino acid isomers.

EXPERIMENTAL

The acrylic acid ammonium salt has been chosen as substrate for the formation of α - or β -alanine in the reaction

The aqueous solution (0,3M) of ammonium salt of acrylic acid was irradiated by high-power picosecond fourth-harmonic pulses of YAG: Nd³⁺ laser with $\lambda = 266$ nm, energy of 1 mJ, duration of 30 ps and repetition frequency of 0,5 Hz.

The solution was put into the 1 ml throughflow quartz cell. The irradiation was carried out at continuous stirring away from air for 1 hour. The local heating of the sample during a pulse is estimated to be several degrees that rules out thermochemical reactions.

The excitation wavelength coincided with the long-wave wing of ammonium acrylate absorption band, the absorption cross-section being equal to $8 \cdot 10^{-18} \text{ cm}^2$. The photoproducts formed do not absorb the laser radiation.

The amino acid analysis of the photoproducts was carried out after extracting the NH_2 -containing fraction with the use of an ion exchange column ("DOWEX-50 $\times$ 8"), a Contron type amino acid analyzer as well as electrophoresis.

RESULTS AND DISCUSSION

The composition of photoproducts was dependent on laser intensity, with the irradiation dose being kept constant.

After comparatively high-intensity irradiation ($J = 3 \times 10^9 \text{ W/cm}^2$) we detected the amino acids, namely α -alanine with the quantum yield 0,015% and β -alanine with the quantum yield of 0,75% as well as polymer-like product.

The polymer, a water-soluble viscous product, was separated together with the amino acid fraction in an ion-exchange column, its quantity being equal approximately to 1,2% by weight. The acid hydrolysis of the amino acid fraction led to a slight increase in the amino acid content in the sample. Thus, the amount of the amino acid residues entering into the oligomer composition and linked by the peptide bond is not large, and polymerization apparently proceeded through the $\text{C}=\text{C}$ bond of acrylic acid, with ammonia being added to the free end vinyl groups of the polymer chain to form a polymer product of a complex structure.

Reducing the laser intensity down to the range $2 \times 10^7 \div 8 \times 10^8 \text{ W/cm}^2$ while keeping the irradiation dose unchanged caused the quantum yields of amino acids to drop. The β -alanine quantum yield was estimated to be 0,05% at $I = 2,6 \cdot 10^7 \text{ W/cm}^2$.

In the region of lower laser intensities polymerization occurred to have place giving rise to a product which tends to precipitate when concentration of the solution is rised up by vacuum evaporation.

This fact points to its fairly high molecular weight. Acid hydrolysis did not cause complete dissolution of the polymer. The analysis of the sample showed the polymer to be free of amino groups and peptide bonds.

Thus, at relatively low laser intensities the most likely process is radical polymerization of the acrylic acid through its C=C bond without interaction with ammonia. As the laser intensity is increased up to $I = 3 \times 10^9 \text{ W/cm}^2$ the probability of the two-quantum absorption of light by the singlet-singlet mechanism becomes higher, resulting in excitation of the ammonium acrylate molecule to high-lying electronic states and addition of ammonia. The fact that the quantum yield of β -alanine depends on the laser intensity points to a nonlinear nature of the process that has been already proposed for the similar synthesis of amino acids.⁴

To check up the conclusion that photochemical formation of amino acids is a result of excitation of high lying electronic states of the molecules of ammonium salts of unsaturated acids, the aqueous solution of ammonium acrylate was irradiated with hydrogen lamp producing the vacuum ultraviolet range radiation, $\lambda = 140 \pm 160 \text{ nm}$. As a result a molecule of salt was directly excited to high-lying singlet electronic state by a single VUV light quantum whose energy is approximately the sum of laser light two quanta energy.

The amino acid analysis of the photochemical reaction products produced by irradiating the solution of ammonium acrylate with low-intensity (2 mW/cm^2) VUV radiation revealed only β -alanine with its weight yield of 0,3% after 3,5 hours irradiation.

Note that radical low-intensity photochemical syntheses of amino acids yield, among other photoproducts, predominantly α -alanine along with β -alanine or the α -alanine only. The addition of the amino group towards the β -position at the carbonyl group is characteristic mainly of direct ammonia addition reactions, for example, in thermal reactions.⁵

Thus when the molecules of ammonium salts of α,β -unsaturated acids are excited to higher singlet electronic states, direct interaction of the molecular C=C bond with ammonia, probably through a unimolecular reaction without formation of intermediate products is possible. The mechanism of this reaction may consist of the intramolecular rearrangement of the system of the conjunctive bonds in the strongly excited molecule.

Such a reaction differs significantly from the photochemical syntheses of amino acids via a number of radical reactions as well as from thermal process of addition of unbonded ammonia to the unsaturated bonds. In this point of view the specific features of nonlinear photochemical formation of amino acids from ammonium salts of unsaturated organic acids mentioned above and predominantly formation of only one isomer (β -alanine) from ammonium acrylate founded in this work could be explained.

In the case of laser experiments the nature of the photoproducts depends on radiation intensity. It assumes different electronic states of excited molecule as the latter absorbs one or successively two light quanta

While at intermediate intensities of laser irradiation, $2 \cdot 10^7 \div 8 \cdot 10^8$ W/cm², occurs mainly the polymerization of C=C bond of acrylic acid probably from triplet excited states, at higher intensities the absorption of the second quantum at the transition $S_1 \longrightarrow S_N$ and the interaction with ammonia become probable.

This interaction gives birth to amino acids and oligomers with the terminal NH₂ groups when high-lying singlet electronic states are excited.

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References

1. C. Sagan, *Nature*, **173**, 417 (1971).
2. A. P. Deschreider, *Nature*, **182**, 528 (1958).
3. R. Cultera and G. Ferrari, *Ann. Chemica*, **47**, 1321 (1957); **48**, 1410 (1958).
4. V. S. Letokhov, Yu. A. Matveetz, V. A. Semchishen and E. V. Khoroshilova, *Appl. Phys.*, **B-26**, 243 (1981).
5. E. V. Khoroshilova, N. P. Kuzmina, V. S. Letokhov, Yu. A. Matveetz, *Appl. Phys.*, **B-31**, 145 (1983).
6. Weygand-Hilgetag, *Organisch-Chemische Experimentierkunst* (I. A. Barth, Verlag/Leipzig, 1964).