CHEMISTRY LETTERS, pp. 687-690, 1980.

THE FORMATION OF α- AND β-ALANINE BY THE INSERTION OF NH($^1\Delta$) RADICALS INTO THE C-H BONDS OF PROPIONIC ACID

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The formation of α- and β-alanine in the photolysis of hydrogen azide in propionic acid was confirmed by the NMR spectra. The yield ratios, alanine/nitrogen and β/α in alanine were found to be 0.4 and 1.5, respectively, suggesting that NH($^1\Delta$) radicals insert into the C-H bonds of propionic acid.

Early in 1960's, the insertion reactions of O(^1D) atoms and $CH_2(^1A_1)$ radicals attracted considerable interests of many chemists.$^{1,2)}$ Since then, NH($^1\Delta$) radicals, which are isoelectronic with O and CH_2, were expected to react with hydrocarbons in the same manner, and a number of investigations have been carried out; however, most of the experiments were unsuccessful to observe the formation of NH-containing products. Recently we studied this type of reaction in liquid phase, i.e., the photolysis of hydrogen azide in liquid ethane, propane, and isobutane at low temperatures, and observed the high yields of amines.$^{3,4)}$ In the case of propane, the yield of n-propylamine was 1.6 times that of isopropylamine. Similarly in the case of isobutane, the formation of isobutylamine was observed with t-butylamine. These results suggest that the main reaction between NH($^1\Delta$) radicals and saturated hydrocarbons is the so-called insertion reaction.

On the basis of this success, we have studied the photolysis of hydrogen azide in propionic acid, and found the formation of α- and β-alanine with a high yield.

Hydrogen azide was synthesized by the reaction of sodium azide with stearic acid, and dried with phosphorus pentoxide. The reaction cell is a Pyrex tube, 10 mm in diameter, in which 2 cm^3 propionic acid and a small amount of hydrogen azide were introduced in vacuo. A medium-pressure mercury lamp was used to illuminate the reaction cell through a transparent quartz-Dewar-flask filled with distilled water at 25°C. Since a Pyrex tube was used as the reaction cell, the effective wavelength was longer than 300 nm.

After the irradiation, the product non-condensable at -196°C was collected with a Toepler pump and its amount was measured with a gas burrett. The mass spectrometric analysis showed that the product is exclusively nitrogen. To separate alanine from the solution, the condensable part was evacuated at room temperature. The white solid left in the tube was subjected to the analysis of NMR (JEOL FX 100). The NMR spectra were obtained in the solution of deuterium oxide. To measure the concentration of alanine, a known amount of maleic acid was dissolved in the solution.

Table 1 summarizes the yield ratios of α- and β-alanine to nitrogen as a function of the initial concentration of hydrogen azide in propionic acid. Evidently the β/α ratio in alanine produced is 1.5, independent of the concentration of hydrogen azide.

Table 1. The ratios of the yields of α- and β-alanine to that of nitrogen in the photolysis of hydrogen azide in propionic acid.

Run No.	HN_3 mol/dm^3	Irradiation time h	α-alanine/N_2	β-alanine/N_2
1	0.10	3	0.19	0.25
2	0.10	2	0.13	0.21
3	0.10	1	0.20	0.32
4	0.05	3	0.11	0.18
5	0.05	2	0.16	0.24
		Mean	0.16 ± 0.04	0.24 ± 0.05

In order to explain these experimental results, we assume the following reaction mechanism, which is similar to that proposed for the photolysis of hydrogen azide in liquid ethylene.5)

$$HN_3 + h\nu \rightarrow NH(^1\Delta) + N_2 \quad (1)$$

$$NH(^1\Delta) + CH_3CH_2COOH \rightarrow CH_3CHNH_2COOH \quad (2)$$

$$\rightarrow CH_2NH_2CH_2COOH \quad (3)$$

$$\rightarrow NH(^3\Sigma) + CH_3CH_2COOH \quad (4)$$

$$NH(^3\Sigma) + HN_3 \rightarrow NH_2 + N_3 \quad (5)$$

$$NH_2 + HN_3 \rightarrow NH_3 + N_3 \quad (6)$$

$$2\ N_3 \rightarrow 3\ N_2 \quad (7)$$

Reaction 4 is the quenching of $NH(^1\Delta)$ by propionic acid. In the present experiment, ammonia could not be analyzed since it was difficult to isolate it from propionic acid. If ammonia is formed, ammonium propionate may be formed. It was confirmed that a small amount of ammonium propionate, if present in propionic acid, is evacuated together with propionic acid.

According to the above mechanism, the quantum yields of α- and β-alanine (ϕ_α and ϕ_β) and of nitrogen (ϕ_{N_2}) should have the following relation:

$$\phi_{N_2} = 4 - 3(\phi_\alpha + \phi_\beta)$$

Experimentally we obtained:

$$\phi_\alpha/\phi_{N_2} = 0.16 \quad \text{and} \quad \phi_\beta/\phi_{N_2} = 0.24.$$

Consequently, $\phi_\alpha = 0.29$ and $\phi_\beta = 0.43$.

More than 70% of the reactions of $NH(^1\Delta)$ radicals with propionic acid lead to the formation of alanine. The triplet state of NH radicals seems to be inactive to propionic acid. The similar observation was made for the reactions of $NH(^3\Sigma)$ radicals in ethylene and propylene.5) As has been shown above, the ratio of ϕ_β/ϕ_α was 1.5; this fact strongly suggests that the insertion of $NH(^1\Delta)$ radicals into the C-H bonds at room temperature is irrespective of the bond strength of the C-H bonds, although we have to wait for the more quantitative measurements using a variety of solvents, before we conclude.

As the solvent, we also tried to use acetic acid in place of propionic acid and found the formation of glycine as the product. Probably many kinds of amino acids can be synthesized by the similar method.

The genesis of amino acids is one of the problems connected to the origin of life. The $^1\Delta$ state of NH radicals is known to be produced in the discharge and in the vacuum-ultra-violet photolysis of ammonia; therefore, the insertion of NH radicals into the C-H bonds of acids might have been an important process for the formation of amino acids on the primitive earth.

The authors are much obliged to Professors Takeshi Nakai and Yoshihiko Morooka of this Institute for the NMR measurement.

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(Received March 29, 1980)