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CONCERNING THE MECHANISM OF PHOTOLYSIS OF N-2,4-DINITROPHENYL-α-AMINO-ACIDS

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Photolysis of 2,4-dinitrophenyl- (DNP-) α-amino-acids involves decarboxylation with intramolecular oxygen transfer from the ortho-nitro group. For amino-acid derivatives the reaction is pH-dependent, giving 6-nitrobenzimidazole 1-oxides at pH 2-4[1], and 4-nitrosoaniline and an aldehyde at other pH values[2]. Hydroxy-acid analogues give 4-nitro-2-nitrosophenol in the pH range 1-12[3]. It is postulated that decarboxylation depends upon oxygen-transfer, which either precedes it[4] or accompanies it concertedly[2c]. Such mechanisms cannot explain the photodecarboxylation of solid DNP-α-amino acids when the ortho-nitro group remains unaffected[5]. To obtain further evidence in this matter we studied the photochemical behaviour of p-nitrophenylvaline, in which no intramolecular oxygen transfer is possible.

In 50 μmolar solution (0.1 M phosphate buffer, pH 6.0), p-nitrophenylvaline rapidly decomposed under conditions described for analytical photolysis[2c]. The resulting solution had λ_{max} 234, 413 nm, consistent with formation of N-isobutyl-p-nitroaniline, and suggesting that simple photodecarboxylation had occurred. In preparative runs the compound (0.7 g.) in pH 6 buffer (700 ml.) was irradiated as previously described[2c]. Volatile products were continuously removed by nitrogen which then passed through 2,4-dinitrophenylhydrazine solution and barium hydroxide solution. After 3 hours no further spectral change occurred; the lamp was extinguished and nitrogen passed for a further 18 hours. The reaction yielded barium carbonate (0.33 g.), isobutyraldehyde 2,4-dinitrophenylhydrazone (0.19 g.) and, from the ethyl acetate extract of the reaction mixture, a yellow crystalline product

(0.28 g.), m.p. 144-145°, with infrared and ultraviolet spectra indistinguishable from those of p-nitroaniline. Thin-layer chromatography (silica gel, benzene) gave a strong spot with the same R_F as authentic p-nitroaniline; only traces of other aromatic compounds were present. The recrystallized material had m.p. and mixed m.p. 147-148°.

These results demonstrate rapid photodecarboxylation in a nitro-arylamino acid where no ortho-nitro group participation is possible. They thus call into question the validity of mechanisms proposed for DNP-amino acid photolysis, which invoke such participation as a mechanistic necessity, and support the original contention[2c] that the primary chemical event is decarboxylation. The product would then be an electronically excited N-alkylaniline which, in the case of dry DNP-amino acids, would collapse to the photostable ground state. In solution a pH-dependent intramolecular oxygen transfer would ensue. With p-nitrophenylvaline in dilute solution the excited intermediate may collapse to the photostable N-isobutyl-p-nitroaniline; in more concentrated solution it would be subject to intermolecular oxidation.

In p-nitrophenylvaline, and by implication in photolabile DNP-compounds, the carboxyl group can accordingly not be regarded as insulated from the chromophore, and the structure normally written for such compounds does not adequately reflect their properties.
In view of the photolability of the solid DNP-α-amino acids, their structural study by X-ray crystallography might help to solve this problem.

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