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Biocatalytic Formation of Industrial Nitriles from Biomass

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PURPOSE OF THE ABSTRACT

Biocatalytic Formation of Industrial Nitriles from Biomass
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The use of hydrocarbons in petrochemistry requires the introduction of functionality to make chemical products. Such processes are multistep and often require large amounts of energy and co-reagents. This is especially true for nitrogen containing chemicals where ammonia is used. Research is being carried out into the conversion of amino acids from protein-rich waste streams into bulk chemicals. An example is glutamic acid (Glu)[1] which can be used for the syntheses of N-succinonitrile[2] and acrylonitrile[3] via 3-cyanopropanoic acid (CPA). CPA can be chemically produced using NaBr and excess NaOCl[2,3]. However, salt formation and the need to cool the reaction results in undesirable economic and ecological effects. An alternative conversion of Glu to CPA is via enzymatic oxidative decarboxylation using vanadium chloroperoxidase (VCPO), H2O2 and NaBr as a vehicle to produce HOBr[4].

Here we explore the role of the halides and their concentration on similar amino acids and the consequences of this on reactivity and selectivity. It was found that the C chainlength of the side chain influences the conversion and selectivity. For example, using VCPO and low NaBr concentrations (0.5 mM), Glu is converted to CPA with high conversion and selectivity. Surprisingly, under the same conditions, aspartic acid (Asp), leads to both low conversion and selectivity. Intra- and intermolecular interactions are believed to stabilize Asp. On increasing the NaBr concentration, both Glu and Asp can be converted with high conversion and selectivity to the desired product. The conversion and selectivity can be modified as a function of NaBr concentration but not the type of halide. This suggests that not only is NaBr in the formation of HOBr, but interacts with the amino acid probably disrupting the intra- and intermolecular interactions which influences the conversion of amino acids into nitriles.

[1] Lammens et al., Biomass & Bioenergy 44 (2012) 168. [2] Lammens et al., ChemSusChem 4 (2011) 785. [3] Le Nôtre et al, Green Chem. 13 (2011) 807. [4] But at al., ChemSusChem 5 (2012) 1199.

FIGURES

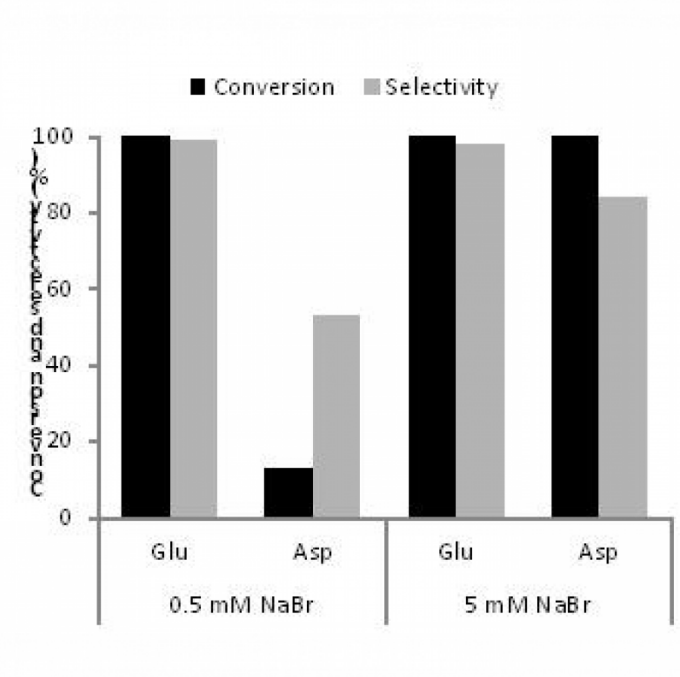

FIGURE 1

Conversion and selectivity

Conversion and selectivity as function of NaBr concentration for Glu to CPA and Asp to 2-cyanoacetic acid. Reaction conditions: 5 mM amino acid, 16 mM H2O2/h, 0.36 U/mL VCPO, 0.5 and 5 mM NaBr, pH=5.6, room temperature, 1 hour.

FIGURE 2

KEYWORDS

biocatalysis | nitriles

BIBLIOGRAPHY

[1] Lammens et al., Biomass & Bioenergy 44 (2012) 168. [2] Lammens et al., ChemSusChem 4 (2011) 785. [3] Le Nôtre et al, Green Chem. 13 (2011) 807. [4] But at al., ChemSusChem 5 (2012) 1199.