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# Hydrolysis of Cinnamaldehyde in Aqueous Solution at Room Temperature Catalyzed by Amino Acids

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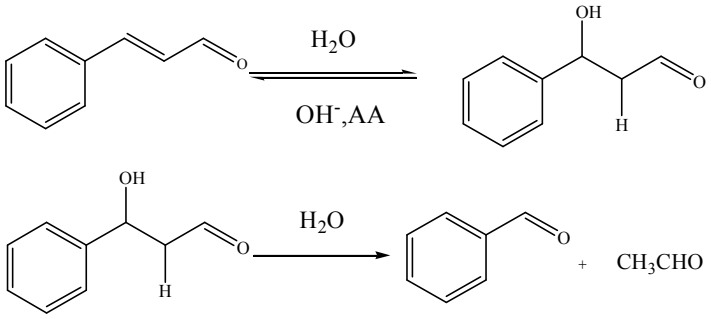
**Abstract:** The hydrolysis of cinnamaldehyde in aqueous solution catalyzed by amino acids has been investigated. Eight amino acids e.g. glycine, proline etc. have been employed as the small molecular organocatalysts. The effect of reaction time, temperature, buffer concentration on the reaction has been studied. Spectroscopic analysis indicated the reaction product is 3-hydroxy-3-phenylpropanal.

Small molecule organocatalysis is one of the hot pots of organic chemistry in recent years. Amino acid organocatalysts have been intensively studied currently because its features e.g. non-toxic, good economics and reusability, easy separation, high selectivity and environment friendly etc [1]. List et al. firstly reported that proline can directly catalyze asymmetric Aldol reaction with enamine mechanism in 2000 [2-3]. After that, the amino acids organocatalysts were widely used in different organic reaction and demonstrated broad application prospects. Some amino acid derivatives have also been developed as organocatalysts [4]. However, simple amino acids organocatalysts have rarely been employed for organic reactions in aqueous system. Wolken and his coworkers [5-6] ever reported the retroaldol condensation of α, β- undaturated carbonyl compounds catalyzed by glycine with high conversion.

In this paper, we reported the hydrolysis reaction of cinnamaldehyde catalyzed by different simple amino acids as demonstrated in Scheme 1. The effects of amino acid structure, reaction time and temperature on the conversion of cinnamaldehyde and reaction selectivity have been investigated.




Scheme 1 Hydrolysis of Cinnamaldehyde in aqueous solution catalyzed by amino acids.

## Experimental method

10ml amino acid/NaOH-buffer (pH 10.0) was mixed with 1.2mmol cinnamaldehyde at 30˚C in a 50ml round bottom flask equipped with magnetic stirrer. The conversion of the cinnamaldehyde after 24h was monitored by GC.

GC analysis was performed on a SP-6890 Gas Chromatogram (Lunan Ruihong Instrument, China) equipped with SE-54 column (30m×0.25mm×0.25μm) and a FID detector. The temperature of column, injector and detector are 180, 200 and 200℃, respectively. 1μL of sample was injected for GC analysis. Agilent 6120 LC/MS system (Agilent, USA) was employed for LC/MS analysis of nonvolatile products. An Inertsil/Wondasil-C18 Column (5μm, 4.6×250mm) column was used with 95% methanol as mobile phase and 1μL of sample injected.

## Results and Discussion

### The amino acid structure on the conversion of cinnamaldehyde

Eight different amino acids e.g. L-glutamate (Glu), phenylalanine (Phe), L-serine (Ser), L-glycine (Gly), L-leucine (Leu), L-proline (Pro), 4 - hydroxy-L-hydroxyproline (Hyp) and L-lysine (Lys) have been employed as the organocatalyst for the hydrolysis of cinnamaldehyde in aqueous solution. The convension and selectivity of the reaction with different amino acid organocatalyst were shown in Table 1.

In the absence of amino acid, cinnamaldehyde can not convert to any product at 30$^{o}$C. The same phenomenon was observed while the reaction was catalyzed by sodium acetate or propylamine. However, over 90% of the cinnamaldehyde was converted with the help of amino acids. Therefore, the Synergistic effect of amino and carboxylic groups of amino acids is important for the reaction.

Table 1 Hydrolysis of cinnamaldehyde catalyzed by different amino acids*

| Name | Glu | Phe | Ser | Gly | Leu | Pro | Hyp | Lys |
|---|---|---|---|---|---|---|---|---|
| Isoelectric point | 3.22 | 5.48 | 5.68 | 5.97 | 5.98 | 6.30 | 6.33 | 9.74 |
| Conversion（%） | 87.4 | 98.4 | 86.6 | 98.7 | 98.2 | 99.2 | 99.5 | 99 |
| Selectivity for benzaldehyde (%) | 2 | 2 | 7.4 | 10 | 5.4 | 22.4 | 7.9 | 4 |

* Reaction conditions: cinnamaldehyde (1.2 mmol), catalyst buffer solution (0.5M,10ml,pH=10.0), 30°C, 24h.

**The effect of reaction time**

The dependence of conversion of cinnamaldehyde on reaction time was shown in Fig. 1.

The conversion of cinnamaldehyde was gradually increased with prolonging reaction time. While Hyp and Pro was used as catalyst, the conversion of cinnamaldehyde reached more than 95% within 1 h. For most of the amino acids, the reaction selectivity for benzaldehyde was among 2% -10%, but that for Pro reached 20%. The dependence of catalytic performance and selectivity of different amino acids on the hydrolysis of cinnamaldehyde are under investigation.

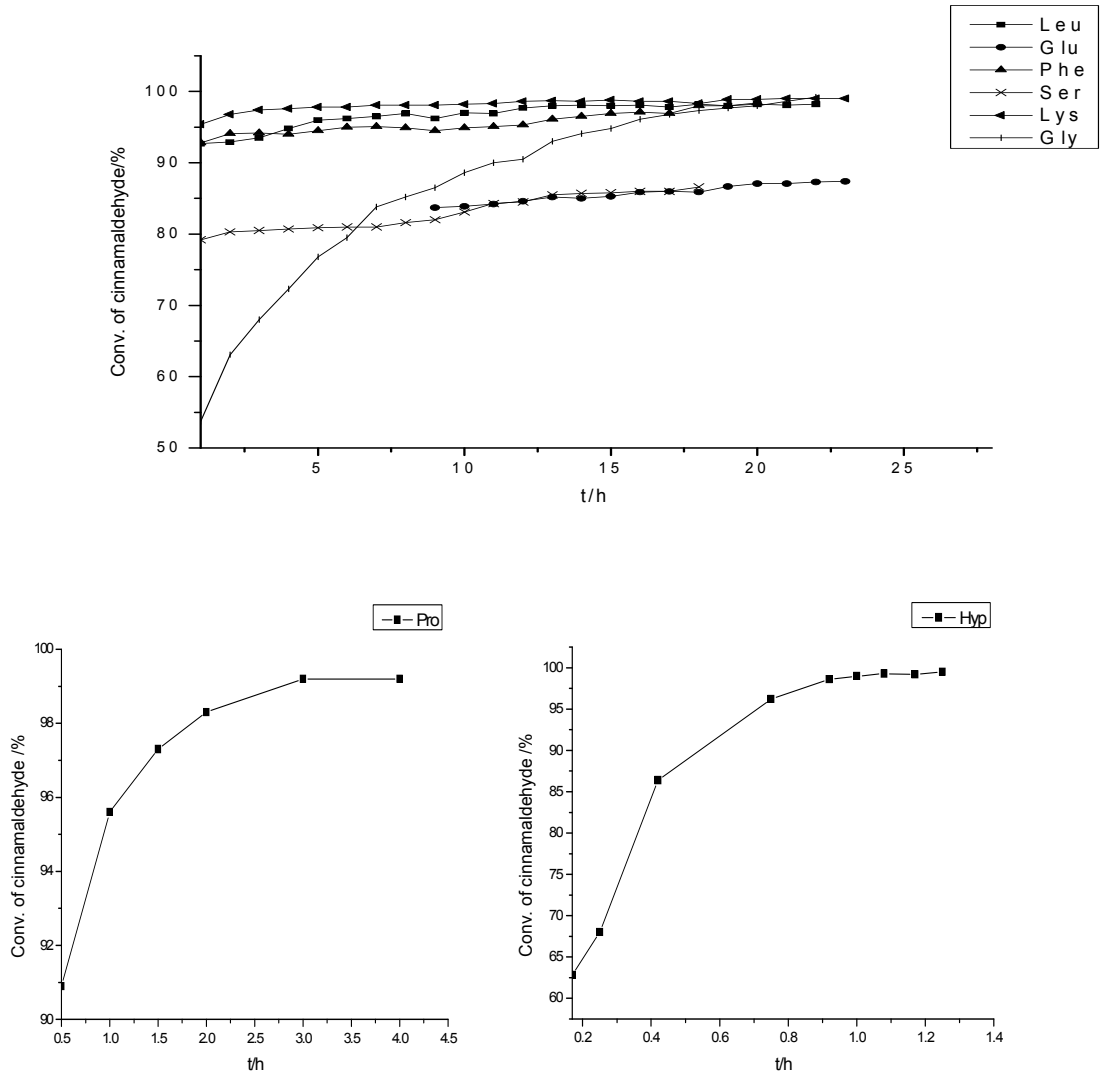



Figure 1 The dependence of conversion of cinnamaldehyde on the reaction time catalyzed by different amino acids

**The effect of reaction temperature**

The effect of temperature on the reaction was determined based on the conversion of cinnamaldehyde at different temperature. The conversion increased slightly with increasing temperature. Therefore, the elevated temperature is conducive to the hydrolysis reaction of cinnamaldehyde.

Table 2 The dependence of conversion of cinnamaldehyde on reaction temperatures

| T/℃ | Glu | Phe | Ser | Gly | Leu | Pro | Hyp | Lys |
|---|---|---|---|---|---|---|---|---|
| 30 | 87.4 | 98.4 | 86.6 | 98.7 | 98.2 | 99.2 | 99.5 | 99 |
| 40 | 92.4 | 98.5 | 94.3 | 100 | 98 | 99.2 | 99.4 | 99.4 |
| 50 | 96.7 | 98.9 | 94.9 | 100 | 98.8 | 99.3 | 99.8 | 99.4 |

**The effect of amino acid concentration on the reaction**

The effects of amino acid concentration on the reaction were studied. The increase of amino acid concentration is favorable to the reaction. The conversion of cinnamaldehyde became constant while the buffer concentration was over 4.5 mol/L for all the amino acids.

**The effect of cinnamaldehyde amount on reaction**

0.5, 1.2 and 2.0 mmol cinnamaldehyde were employed for the hydrolysis. It was interesting to found that the conversion increased with increasing cinnamaldehyde concentration. This is probably because the product, 3-hydroxy-3-phenylpropanal, is water-soluble and can act as surfactant to improve the solubility of cinnamaldehyde so as to accelerate the hydrolysis reaction.

Table 3. Cinnamaldehyde addition on conversion of cinnamaldehyde

| Con.of cinnamaldehyde （%） | Glu | Phe | Ser | Gly | Leu | Pro | Hyp | Lys |
|---|---|---|---|---|---|---|---|---|
| 0.5mmol | 82.8 | 96.5 | 63.9 | 94.6 | 87 | 98.6 | 96.5 | 99.1 |
| 1.2mmol | 87.4 | 98.4 | 86.6 | 95 | 98.2 | 99.2 | 99.5 | 99 |
| 2.0mmol | 88.2 | 98.5 | 95.1 | 96.8 | 98.6 | 99.5 | 99.6 | 99.4 |

**Characterization of product**

HPLC results indicated that the main products with different amino acids were the same. Its molecular weight measured by high-resolution mass spectrometry was 147.0440. The corresponding molecular formula is $C_9H_{10}O_2$. MS, IR and NMR indicated the product is 3-hydroxy-3-phenylpropanal.

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