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Kinetics of non-catalyzed hydrolysis of tannin in high temperature liquid water*

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Abstract: High temperature liquid water (HTLW) has drawn increasing attention as an environmentally benign medium for organic chemical reactions, especially acid-/base-catalyzed reactions. Non-catalyzed hydrolyses of gallotannin and tara tannin in HTLW for the simultaneous preparation of gallic acid (GA) and pyrogallol (PY) are under investigation in our laboratory. In this study, the hydrolysis kinetics of gallotannin and tara tannin were determined. The reaction is indicated to be a typical consecutive first-order one in which GA has formed as a main intermediate and PY as the final product. Selective decomposition of tannin in HTLW was proved to be possible by adjusting reaction temperature and time. The present results provide an important basic data and reference for the green preparation of GA and PY.

Key words: High temperature liquid water, Gallotannin, Tara tannin, Non-catalyzed hydrolysis, Kinetics
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INTRODUCTION

High temperature liquid water (HTLW), as an environmentally benign medium, has drawn increasing attention for use in organic chemical reactions (Akiya and Savage, 2002; Eckert *et al*., 2004; Lu *et al*., 2003). HTLW has a strong tendency to ionize and can act as an acid and/or base catalyst. Additionally, HTLW can dissolve organic substance to some extent, allowing for a homogeneous reaction within an aqueous phase. Extensive researches have been conducted on acid-/base-catalyzed reactions without added acid or base in HTLW (Nolen *et al*., 2003; Sasaki *et al*., 2000; Lu *et al*., 2002).

Gallic acid (GA, 3,4,5-trihydroxybenzoic acid) and pyrogallol (PY, 1,2,3-trihydroxybenzene) are industrially important chemicals widely used in organic synthesis, pharmaceutical, food, and integrated circuit manufacturing (Wang, 1995; Lee, 2000). Industrially, GA is mainly produced from tannin (gallotannin or tara tannin) by acid-/base-catalyzed hydrolysis (Wang, 1995; Chen *et al*., 1995), and then thermally decarboxylated with catalyst to produce PY. However, the process results in severe environmental pollution. Therefore, it is desirable to develop an environmentally benign preparation process of GA and PY.

Currently, non-catalyzed hydrolyses of gallotannin and tara tannin in HTLW for the simultaneous preparation of GA and PY are under investigation in our laboratory. The present work is mainly to study the kinetics of non-catalyzed hydrolyses of gallotannin and tara tannin in HTLW so as to provide important basic data for the development of the technology.

MATERIALS AND METHODS

Materials

Gallotannin and tara tannin (≥99% purity) were obtained from Linyuan Chemical Company of Zunyi,

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China. Tannin, composed by tannic acid with different molecular weight, is difficult to be quantified. As an ester, tannin can be totally hydrolyzed with hydrochloric acid to produce GA and glucose/quinic acid (Liu and Zhang, 2002). Therefore, tannin content can be measured as GA by HPLC after acid hydrolysis (Nakamura *et al*., 2003). Using this method, tannin contents of gallotannin and tara tannin are 4.17 mmol/g and 4.32 mmol/g, respectively.

GA, PY and phosphoric acid were obtained from Shanghai Chemical Reagent Co., China. All the reagents were of analytical grade (≥99% purity) and used without further purification. HPLC grade methanol and acetonitrile were obtained from Merck (Germany).

Apparatus

Fig.1 shows a schematic diagram of the experimental setup, which mainly consists of a high-pressure autoclave (530 ml), a plunger pump, a mechanical impeller and a sampling line. The sampling line includes a high-pressure valve V_6 and a cooler. The tubing is 0.16 cm o.d. and 0.076 cm i.d. (SUS316) with a volume of 0.60 ml. The apparatus exhibits the following features: temperature up to 593.15 K, pressure up to 20 MPa, good temperature control of ±1 K, on-line sampling, and resistance to corrosion because the autoclave is made of titanium alloy TC4.

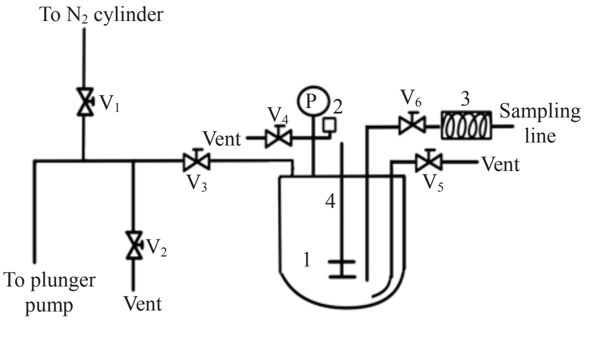


Fig.1 Schematic diagram of the experimental apparatus
1: Reactor; 2: Safety valve; 3: Cooler; 4: Mechanical impeller; V_1~V_6: High pressure valves; P: Pressure guage

Experimental procedures

The typical kinetic experiment process was as follows. Firstly, the system was degassed with a vacuum pump and then filled with high-purity nitrogen. Then, 350 ml of degassed deionized water was injected through valve V_3 by using a plunger pump. Next, the system pressure was increased to 3 MPa by high-pressure nitrogen from a cylinder. After the temperature inside the reactor had reached the reaction temperature, 30 ml of 38 mg/ml gallotannin/tara tannin-water mixture or 20 mg/ml GA-water mixture was quickly injected by the plunger pump through valve V_3, and the line was rinsed with 20 ml of degassed deionized water. The temperature inside the reactor reached the reaction temperature within several minutes. Finally, samples were collected at certain reaction time. The system pressure was maintained at 5 MPa during the whole reaction process, and the reaction mixture was constantly agitated at 200 r/min using a mechanical impeller.

After 1~2 ml of solution had been vented to rinse the sample line, about 5 ml of solution was quickly depressurized through valve V_6, cooled and collected. Then 2 ml of sample solution was measured, diluted and analyzed. The pressure drop (0.1~0.2 MPa) during sampling was compensated by high-pressure N_2.

Analysis

All the samples were quantitatively analyzed by reverse-phase HPLC (Agilent 1100 series) (Nakamura *et al*., 2003; Shahrzad and Bitsch, 1998). The HPLC column was a Diamonsil C18 (250 mm×4.6 mm, 5 μm, Dikma Technologies, USA). Phosphoric acid (8.5×10^{-3} mol/L)-methanol-acetonitrile (80:10:10, v/v/v) was used as the mobile phase at a flow rate of 0.8 ml/min. Column temperature was 298.15 K, injection volume was 5 μl, and the detection wavelength was 202 nm.

RESULTS

Hydrolysis products

A typical HPLC chromatogram of the reaction products of tannin hydrolysis is shown in Fig.2. The two main chromatographic peaks were confirmed to be GA and PY by comparing their retention time with those of standards.

Material balance

Considering that GA can be decarboxylated to produce PY in HTLW, tannin contents were determined as GA and PY by HPLC after non-catalyzed hydrolysis. The results are listed in Table 1 with tannin content determined as GA by acid hydrolysis. Comparing the values determined by two methods of acid and non-catalyzed hydrolyses in HTLM, we found that GA liberated from tannin either exists as GA or is converted into equimolecular PY in experimental temperature range.

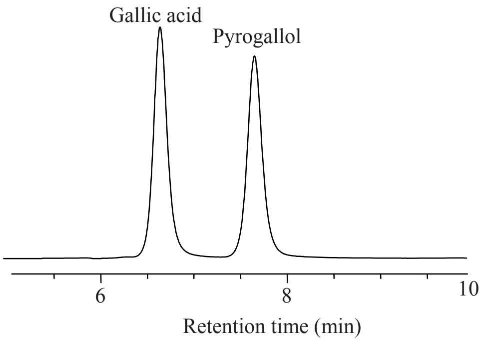


Fig.2 Typical HPLC chromatogram of the reaction products

Table 1 Tannin content determined by non-catalyzed hydrolysis in HTLW and acid hydrolysis

Method	T (K)	Tannin content as GA and PY (mmol/g)	
		Gallotannin	Tara tannin
Acid hydrolysis	373.15	4.17±0.08*	4.32±0.10*
Non-catalyzed hydrolysis in HTLW	413.15	4.20±0.06	4.34±0.12
	423.15	4.21±0.09	4.31±0.06
	433.15	4.16±0.12	4.27±0.08
	443.15	4.19±0.11	4.24±0.13
	453.15	4.11±0.08	4.29±0.14

Data expressed as mean±*SD*; * Tannin content as GA (mmol/g)

Effect of the initial concentration of tannin on its hydrolysis

The effect of the initial concentration of tannin on GA yield was investigated for gallotannin and tara tannin, respectively. The reactions were carried out at temperature of 443.15 K and under pressure of 5 MPa. As an illustration, the corresponding results for gallotannin are depicted in Fig.3. The results demonstrate that the initial concentration of tannin has little effect on its hydrolysis for both tannins in the experimental concentration range (1.5~5.7 mg/ml). The concentrations of gallotannin and tara tannin were both selected as 2.86 mg/ml in the following experiments.

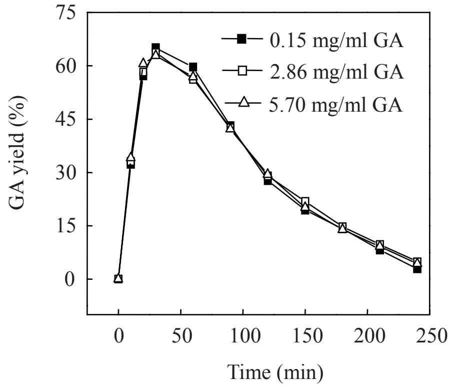


Fig.3 Effect of the initial concentration of gallotannin on GA yield

Reproducibility of the hydrolysis of tannin

The reproducibility of the hydrolysis of tannin was investigated for gallotannin and tara tannin, respectively. The reactions were carried out at temperature of 443.15 K, at concentration of 0.15 mg/ml and under pressure of 5 MPa. The corresponding results for gallotannin are plotted in Fig.4, showing that the yield measurement could be repeated.

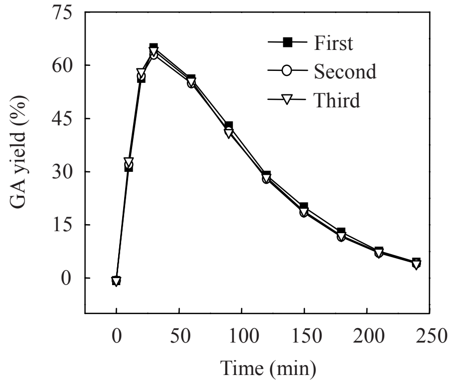
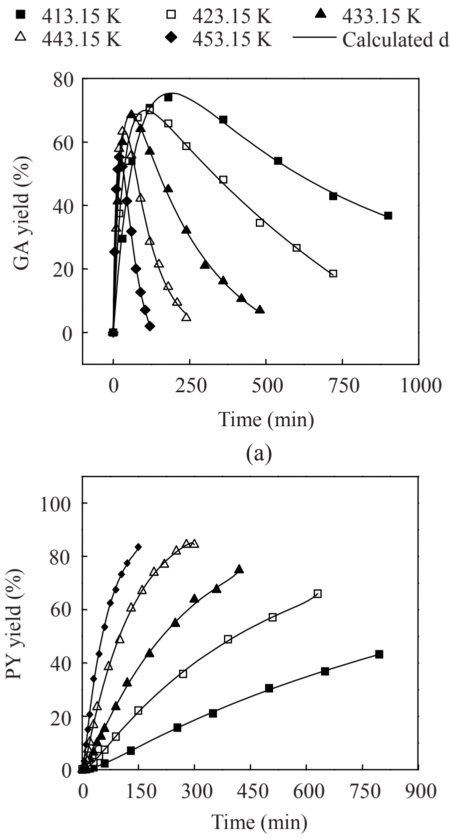


Fig.4 Reproducibility tests for gallotannin hydrolysis in HTLW

Hydrolysis kinetics of tannin

The effect of the reaction temperature on the yield of GA and PY at different residence time was studied for both tannins. The reaction pressure was controlled at 5 MPa. Figs.5a and 5b show the experimental results of gallotannin. The intermediate GA might have undergone a decarboxylation which produces PY. Moreover, the reaction rates of tannin hydrolysis and decarboxylation increase monotonically with increasing temperature.



(a)

(b)

Fig.5 Effect of the reaction temperature on (a) GA yield and (b) PY yield

Decarboxylation of GA in HTLW

As indicated in above results, tannin can be hydrolyzed in HTLW to give two main products, GA and PY. In order to clarify the kinetics of tannin hydrolysis in HTLW, the kinetics of GA decarboxylation in HTLW were investigated separately. The reaction pressure was maintained at 5 MPa, and the initial concentration of GA is 1.48 mg/ml. The results in Figs.6a and 6b indicate that PY is the only product of GA decarboxylation, and that the reaction rate increases monotonically with increasing temperature.

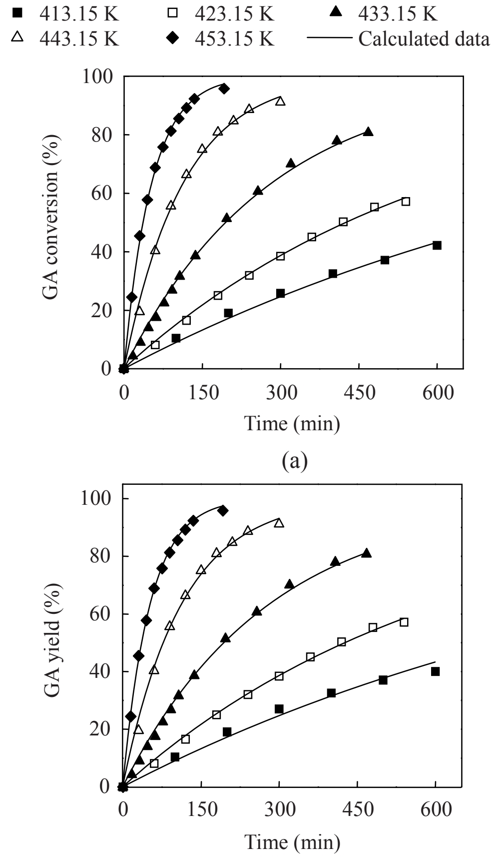
Data analysis

The possible reaction scheme of tannin hydrolysis is shown in Fig.7. Given that tannin hydrolysis is a consecutive first-order reaction, we obtained the following expressions:

$$y=b[\exp(-k_2t)-1]+[ak_1/(k_2-k_1)][\exp(-k_1t)-\exp(-k_2t)], \qquad (1)$$

$$y=c-a\exp(-k_1t)-b\exp(-k_2t)-[ak_1/(k_2-k_1)][\exp(-k_1t)-\exp(-k_2t)], \qquad (2)$$

where y in Eqs.(1) and (2) represents the yields of GA and PY, respectively; k_1 and k_2 represent the reaction rate constants of tannin hydrolysis and GA decarboxylation, respectively; and a, b and c are parameters; t is reaction time.



(a)

(b)

Fig.6 Effect of the reaction temperature on (a) GA conversion and (b) GA yield

Eqs.(1) and (2) were adopted to correlate experimental data of tannin hydrolysis, and the calculated curves are shown in Figs.5a and 5b. There is a good agreement between the experimental data and the calculated curves. For GA decarboxylation, the equation $y=1-\exp(-k_2t)$ was used to correlate the experimental data, and the calculated curves are shown in Figs.6a and 6b, suggesting that the equation fits the data very well.

The evaluated rate constants for tannin hydrolysis and GA decarboxylation, together with error limits

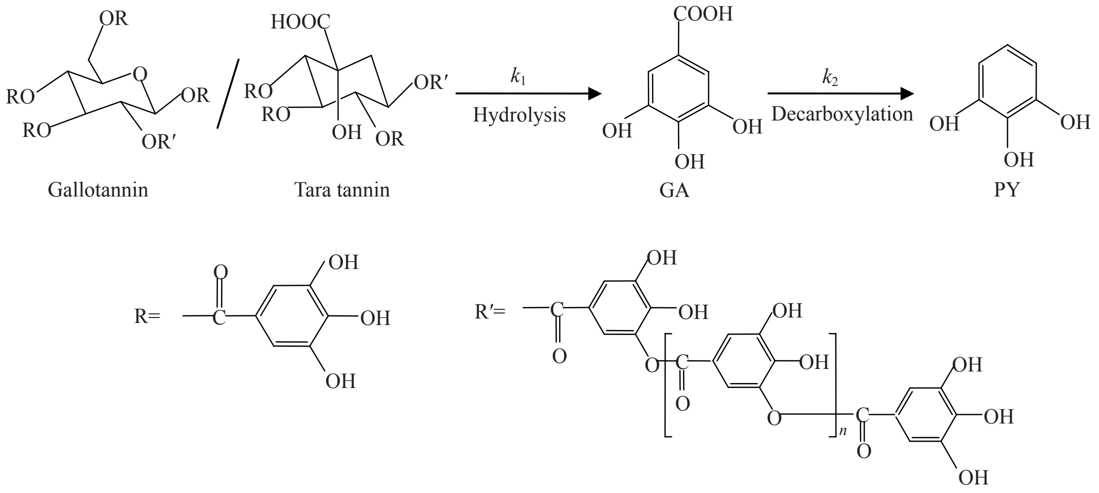


Fig.7 Proposed reaction scheme for the hydrolysis of tannins

using the 95% confidence level at different temperatures are listed in Table 2. From Arrhenius plots, the apparent activation energies were evaluated as (63.9±6.2) kJ/mol for gallotannin hydrolysis and (96.0±7.5) kJ/mol for tara tannin hydrolysis. The apparent activation energies of GA decarboxylation were calculated as (126.6±11.3), (112.7±8.0) and (116.6±6.3) kJ/mol, respectively.

DISCUSSION

Gallotannin and tara tannin can be hydrolyzed to produce GA and PY without any catalyst in HTLW. As temperature increases, the concentrations of H^+ and OH^- increase, which can catalyze chemical reactions. Therefore, the reaction temperature has significant effect on the tannins hydrolysis and GA decarboxylation.

As shown in Table 2, all the reaction rates increase monotonically with increasing temperature. Given the experimental error, those values of k_2 calculated for different reactants are essentially the same. The hydrolysis of gallotannin and tara tannin is a typical two-step consecutive reaction. Moreover, the fitting results indicate that every reaction step is of first-order. As the values of apparent energies indicate, reaction temperature has more significant effect on GA decarboxylation than on tannin hydrolysis. Therefore, selective hydrolysis of tannins in HTLW was possible by controlling the reaction temperature and time. In spite of the higher apparent energy, the hydrolysis rate of tara tannin is bigger than that of gallotannin on the same reaction conditions, which might be explained by the catalysis of the carboxyl of tara tannin.

Table 2 Evaluated rate constants at different temperatures for tannin hydrolysis and GA decarboxylation

T (K)	Gallotannin		Tara tannin		GA
	k_1 (min^{-1})	k_2 (min^{-1})	k_1 (min^{-1})	k_2 (min^{-1})	k_2 (min^{-1})
413.15	0.0170±0.0008	0.0007±0.00004	0.0231±0.0015	0.0008±0.00004	0.0008±0.00030
423.15	0.0293±0.0010	0.0017±0.00008	0.0483±0.0023	0.0020±0.00010	0.0019±0.00010
433.15	0.0440±0.0019	0.0039±0.00012	0.0791±0.0041	0.0037±0.00020	0.0040±0.00014
443.15	0.0666±0.0025	0.0084±0.00020	0.1483±0.0070	0.0082±0.00030	0.0080±0.00020
453.15	0.0874±0.0050	0.0186±0.00100	0.2867±0.0013	0.0155±0.00090	0.0177±0.00080

The initial concentrations of tannin and GA were 2.86 and 1.48 mg/ml, respectively; k_1 and k_2 represent the reaction rate constants of tannin hydrolysis and GA decarboxylation, respectively

CONCLUSION

The non-catalyzed hydrolyses of gallotannin and tara tannin in HTLW have been successfully conducted to exploit the environmentally benign preparation of GA and PY. The hydrolysis kinetics of both tannins in HTLW have been investigated for the first time.

The results show that the reaction is a typical consecutive first-order one in which GA formed as a main intermediate and PY as the final product. The reaction temperature shows significant effect on gallotannin and tara tannin hydrolyses and GA decarboxylation.

Those results from our work provide an important basic data and reference for the green preparation of GA and PY, as well as other tannin hydrolysis in HTLW.

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