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Degradation of benzoic acid and its derivatives in subcritical water

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ABSTRACT

In this research, the stability of benzoic acid and three of its derivatives (anthranilic acid, salicylic acid, and syringic acid) under subcritical water conditions was investigated. The stability studies were carried out at temperatures ranging from 50 to 350 °C with heating times of 10–630 min. The degradation of the benzoic acid derivatives increased with rising temperature and the acids became less stable with longer heating time. The three benzoic acid derivatives showed very mild degradation at 150 °C. Severe degradation of benzoic acid derivatives was observed at 200 °C while their complete degradation occurred at 250 °C. However, benzoic acid remained stable at temperatures up to 300 °C. The degradation products of benzoic acid and the three derivatives were identified and quantified by HPLC and confirmed by GC/MS. Anthranilic acid, salicylic acid, syringic acid, and benzoic acid in high-temperature water underwent decarboxylation to form aniline, phenol, syringol, and benzene, respectively.

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1. Introduction

At elevated temperatures the intermolecular hydrogen bonds of water are weakened causing water to become less polar and behave more like an organic solvent [1–3]. With its decreased dielectric constant, surface tension, and viscosity, water under subcritical conditions has a number of applications. One of the major applications is subcritical water extraction. Recent studies clearly demonstrate that subcritical water can be used as an extraction fluid for many classes of organic compounds from a variety of sample matrices including environmental, food, pharmaceutical, and plants [1,2,4–25]. Another main application of subcritical water is subcritical water chromatography where pure water is used as the sole component in the mobile phase to achieve reversed-phase separation [26–40,5]. This green chromatography technique has been extensively investigated in our laboratory [3,26–32,5]. Subcritical water chromatography has also been found promising by other researchers [33–40]. The most obvious advantage of subcritical water extraction and subcritical water chromatography techniques is the elimination or minimization of hazardous organic solvents required in the separation processes.

While these green subcritical water techniques are promising, the stability of analytes under subcritical water conditions needs to be evaluated to ensure the accuracy of subcritical water extraction and chromatography data.

Benzoic acid is mainly used as a preservative in food, cosmetics, and other fields. Benzoic acid derivatives including anthranilic acid, syringic acid, and salicylic acid are found in Chinese medicinal herbs and other plants [41]. As mentioned above, subcritical water extraction has been recently applied to the extraction of herbs [17–25]. The high temperatures used in these herbal extraction methods may cause benzoic acid derivatives to degrade. Our recent solubility study revealed that the solubility of salicylic acid was dramatically decreased at 250 °C [42], which indicated that degradation of salicylic acid in water occurred at this high temperature. Our previous study also showed degradation of terpenes occurred during subcritical water extraction of basil and oregano [17]. Degradation of other analytes in subcritical water was also reported [43–45].

In this research, the temperature effect on the stability of benzoic acid and derivatives in subcritical water was investigated. A mixture of an individual acid and water was heated in a reactor at different temperatures. The experimental temperature ranged from 50 to 350 °C. The kinetic experiments were performed with heating times ranging from 10 to 630 min. The reaction mixtures were then analyzed by HPLC to determine the analyte stability. If a given acid was degraded under certain conditions, the degradation products were identified and quantified by HPLC and confirmed by GC/MS.

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2. Experimental

2.1. Reagents

Benzoic acid, salicylic acid, benzene, sodium phosphate monobasic, and *o*-phosphoric acid 85%, phenol were purchased from Fisher Scientific (Fair Lawn, NJ, USA). Syringic acid and aniline were acquired from Sigma-Aldrich (Milwaukee, WI, USA). Syringol and *m*-cresol were obtained from Acros Organics (Geel, Belgium). Anthranilic acid from Eastman Chemical Company (Kingsport, TN, USA) and HPLC grade methanol from Burdick & Jackson (Morristown, NJ, USA) were also used. Deionized water (18 MΩ cm) was prepared in our laboratory and purged using UHP Grade helium. Acetone was obtained from VWR International, LLC (West Chester, PA, USA).

2.2. Heating of organic-water mixtures

Stainless steel vessels (7.07, 9 cm × 1 cm ID, Raleigh Valve and Fitting Company, Raleigh, NC, USA) were used for heating the mixtures of a given analyte and water.

The reaction vessels were rinsed with acetone and allowed to dry prior to each use. Both ends of each reaction vessel were wrapped with Teflon tape and one end was sealed tightly with an end cap. Approximately 5 mg of anthranilic acid, salicylic acid, syringic acid, or benzoic acid was weighed into each reaction vessel. 5 mL of degassed and deionized water was added to each reaction vessel. The remaining volume of each vessel was left as void during the high-temperature reactions for safety considerations. The open end of each reaction vessel was then sealed tightly with another end cap. The loaded reaction vessels were heated inside a Hewlett-Packard 5890 Series II Gas Chromatograph Oven (Palo Alto, CA, USA). The effect of temperature on organic acid stability in subcritical water was evaluated in triplicate experiments at temperatures of 50, 100, 150, 200, 250, 300, and 350 °C. The effect of heating time on organic acid degradation was determined using 10–630 min.

The loaded reaction vessels were heated from an initial temperature of 25 °C to the desired temperature and held there for the desired period of time. Counting of the heating time began when the oven temperature reached the desired value. After the heating was completed, the vessels were allowed to cool to room temperature and then taken out of the oven.

2.2.1. Sample preparation for HPLC analysis

After the vessels were cooled to the room temperature, each vessel was kept in the upright position and one end cap was removed. The heated mixture in each reaction vessel was transferred into a 10-mL glass vial. Anthranilic acid was used as the internal standard for syringic acid, salicylic acid, and benzoic acid experiments while syringic acid was used as the internal standard for anthranilic acid experiment. To the emptied reaction vessel 1.00 mL of internal standard solution was added to rinse down the sides of the reaction vessel and remove any residue. The internal standard rinse was then transferred into the glass vial containing the reaction mixture. Another 1.00 mL of internal standard solution was added to the emptied reaction vessel to rinse it again and then transferred into the same glass vial containing the reaction mixture. This sample solution was used for HPLC analysis.

2.2.2. Sample preparation for GC/MS analysis

For selected experimental conditions, GC/MS was used to confirm the identity of the degradation products. Experiments were repeated as described above up to the point where the reaction vessels were allowed to cool to room temperature. The reaction mixture in each reaction vessel was transferred into a 10-mL glass vial. To the emptied reaction vessel 2 mL of methylene chloride was added to rinse down the sides of the reaction vessel and remove any residue. The methylene chloride was then transferred into the same glass vial containing the heated reaction mixture. 5.0 μL of an internal standard solution (a neat solution of *m*-cresol) was added to the sample vial and a liquid–liquid extraction was performed. After mixing the two layers, the methylene chloride layer was transferred into a sample vial. Another 2 mL of methylene chloride was added to the vial containing the aqueous reaction mixture. A second liquid–liquid extraction was performed. The methylene chloride layer was combined with the first methylene chloride fraction for GC/MS analysis.

2.3. HPLC analysis

A Waters Corporation gradient HPLC system (Milford, MA, USA) consisting of a 717 plus Autosampler, 2487 Dual Wavelength Absorbance Detector, and 1525 Binary HPLC Pump was used for analysis. Breeze Version 3.30 SPA was used for system control and data acquisition. Separation was achieved on a Phenomenex Synergi Polar-RP column (80 Å, 100 mm × 4.60 mm, 4 μm, Phenomenex, Torrance, CA, USA) maintained at 25 °C.

The mobile phase used was 0.02 *M* sodium phosphate buffer, pH 2.7 (mobile phase A) and methanol (mobile phase B). The gradient was as follows: 75% A for 0–10 min, 70% A for 10–11 min, and 75% A for 11–15 min. The flow rate was set at 1.50 mL/min and injection volume was 10 μL. UV detection was at 254 nm. Two different internal standards as described above were used. Quantification of benzoic acid derivatives and their degradation products was obtained by using calibration curves generated using a series of five standard solutions.

2.4. GC/MS analysis

An Agilent Technologies 6890N Network GC System (Santa Clara, CA, USA) coupled with a JEOL Ltd. JMS-GCmate II MS System (Tokyo, Japan) was used to confirm the identity of the degradation products. Shrader Analytical and Consulting Laboratories, Inc. TSSPro Version 3.0 was used for data acquisition and treatment. The GC capillary column used was an Agilent HP-5MS (5%-Phenyl)-methylpolysiloxane (30 m × 0.250 mm, 0.25 μm film thickness). The carrier gas was helium and the column flow was 1 mL/min. The injection volume was 1 μL. The injection mode was split and the injector temperature was set at 250 °C. The oven temperature profile was as follows: The initial temperature was held at 30 °C for 5.00 min. Then it was increased at 20 °C/min to 250 °C that was held for 5.00 min. The GC interface and the MSD ion chamber were set at 250 °C. The MS solvent delay time was 3 min.

3. Results and discussion

3.1. Temperature effect on the stability of benzoic acid and its derivatives

As shown in Fig. 1, all four acids studied remained stable at temperatures up to 100 °C. Except benzoic acid, the other three acids showed minor degradation at 150 °C. The percent degradation at 150 °C is below 10% and depending on the heating time applied as demonstrated in Fig. 1.

However, the three benzoic acid derivatives showed significant degradation at 200 °C but benzoic acid still remained stable. Fig. 1 also shows the stability trend for the four acids at 200 °C with benzoic acid being the most stable one followed by syringic acid, salicylic acid and anthranilic acid being the least stable one. All three benzoic acid derivatives were almost completely degraded at 250 °C as evidenced in Fig. 1. The relative standard deviation for

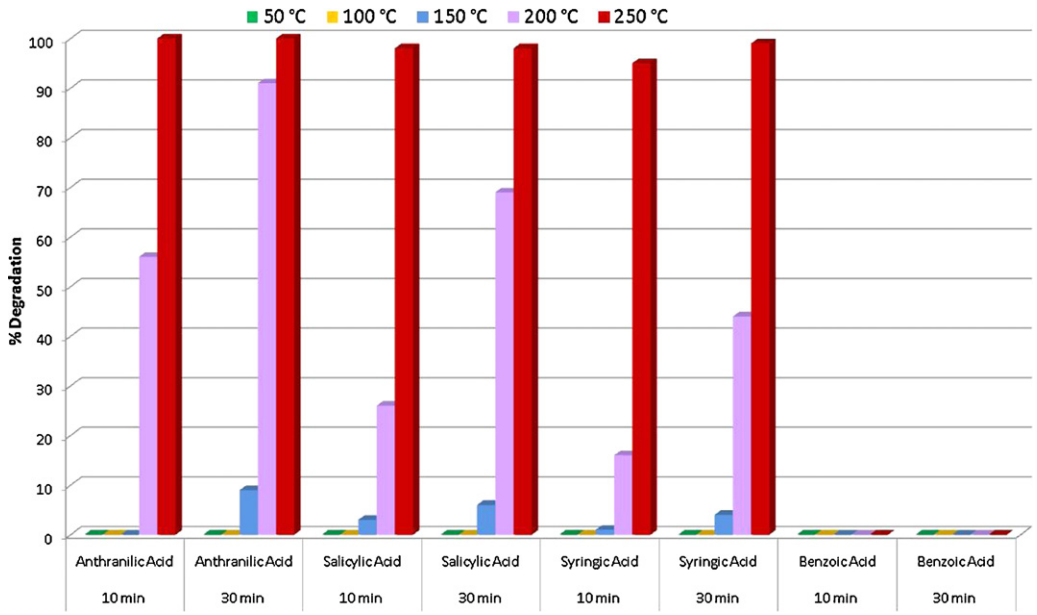

Fig. 1. Effects of temperature and heating time on the stability of benzoic acid and derivatives in subcritical water. Percent degradation was determined by triplicate measurements with relative standard deviation below 8% for all data shown in the figure.

the percent degradation triplicate measurements is below 8% for all data shown in Fig. 1. The chromatograms of the water–benzoic acid derivatives mixtures obtained after heating at 200 and 250 °C are compared in Figs. 2–4. While trace amount of anthranilic acid can still be seen after heating at 200 °C, its peak completely disappeared after heating at 250 °C (Fig. 2).

Please note that benzoic acid remained stable even at 300 °C. Further benzoic acid stability experiments at higher temperatures revealed that only 4% benzoic acid was degraded at 350 °C with a heating time of 10 min as shown in Fig. 5.

3.2. Effect of the heating time on the stability of benzoic acid and its derivatives

Our kinetic study indicated that longer exposure time caused greater acid degradation at a given temperature as shown in Figs. 1 and 5. For example, 56% of anthranilic acid was degraded after heating at 200 °C for 10 min as shown in Fig. 1. However, anthranilic acid degradation increased to 91% by lengthening the heating time to 30 min at the same temperature (Fig. 1). Similar trends were observed for salicylic acid and syringic acid at 150 and 200 °C as depicted in Fig. 1. The stability of benzoic acid was investigated with much longer heating time. As shown in Fig. 5, benzoic acid degradation at 350 °C was intensified from 4% to 46% by increasing the heating time from 10 to 630 min. Fig. 6 shows the chromatograms of the benzoic acid–water mixture after heating at 350 °C for various periods of time.

3.3. Identification and quantification of the degradation products

As discussed earlier, the three benzoic acid derivatives were clearly degraded at 200 °C and higher temperatures. In order to characterize the degradation products, the heated organic-water mixtures at 200 and 250 °C were used for identification and quan-

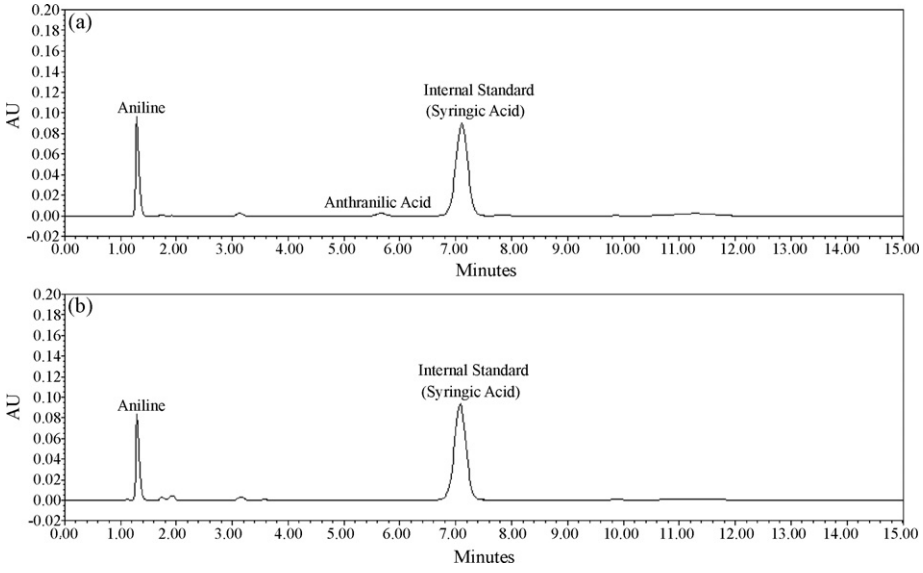

Fig. 2. HPLC chromatograms of the anthranilic acid–water mixture after heating at (a) 200 °C for 30 min and (b) 250 °C for 30 min.

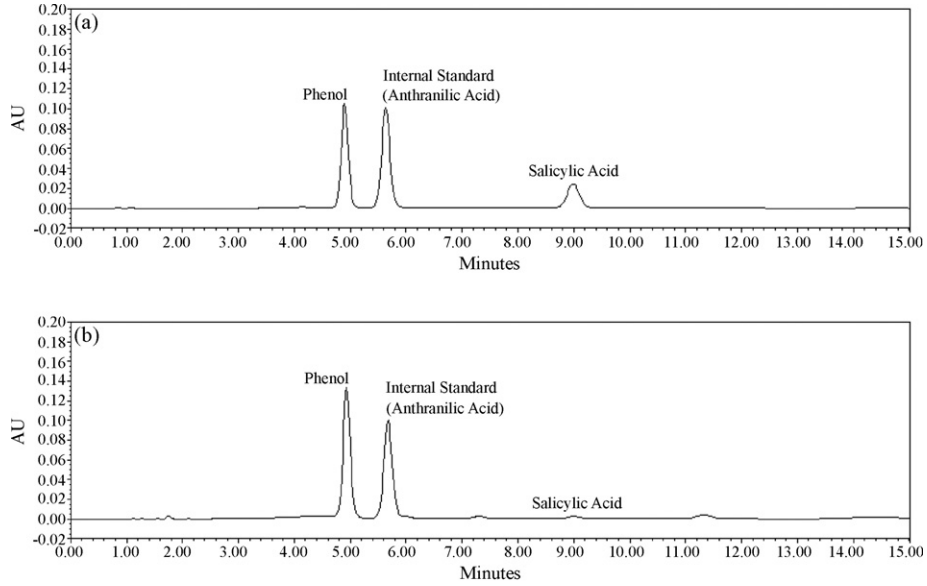

Fig. 3. HPLC chromatograms of the salicylic acid–water mixture after heating at (a) 200 °C for 30 min and (b) 250 °C for 30 min.

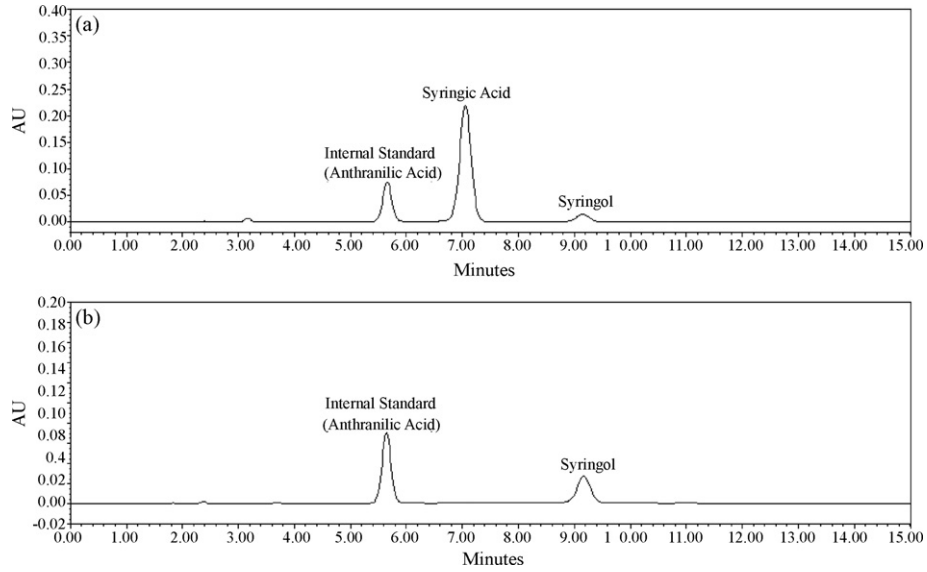

Fig. 4. HPLC chromatograms of the syringic acid–water mixture after heating at (a) 200 °C for 30 min and (b) 250 °C for 30 min.

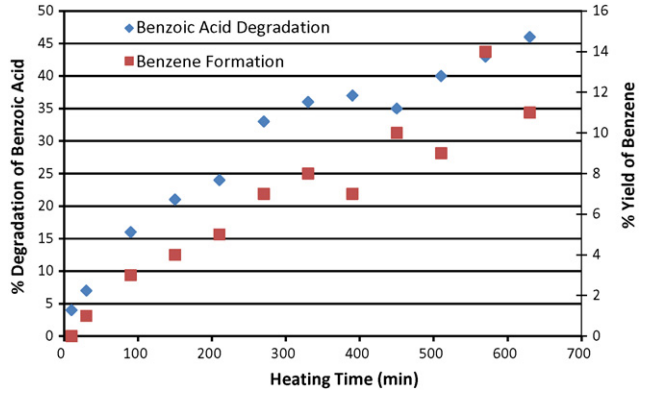

Fig. 5. Effect of heating time on the degradation of benzoic acid and the yield of benzene formation in subcritical water at 350 °C. Percent degradation and percent yield were determined by triplicate measurements with relative standard deviation mostly below 20% for data shown in the figure.

tification of the degradants using HPLC. As shown in Fig. 2, aniline is the main degradation product of anthranilic acid at both 200 and 250 °C. Fig. 3 reveals that phenol is the main degradation product of salicylic acid at 200 and 250 °C. Fig. 4 indicates that syringic acid was converted to syringol at high temperatures. One can easily see the correlation between syringic acid degradation and syringol formation by comparing the chromatograms obtained at 200 and 250 °C as shown in Fig. 4(a) and (b). The higher the degradation of syringic acid, the greater the yield of syringol. As we already know, benzoic acid is much more stable in subcritical water than its derivatives. Therefore, the identification of benzoic acid degradation products was performed using benzoic acid–water mixtures after heating at 350 °C. As shown in Fig. 6, benzene is the main degradation product of benzoic acid in subcritical water.

The identification of these degradation products was further investigated by GC/MS analysis. The GC/MS analyses based on both GC retention and the MS spectra of the degradants confirmed the degradation products determined by HPLC as discussed above.

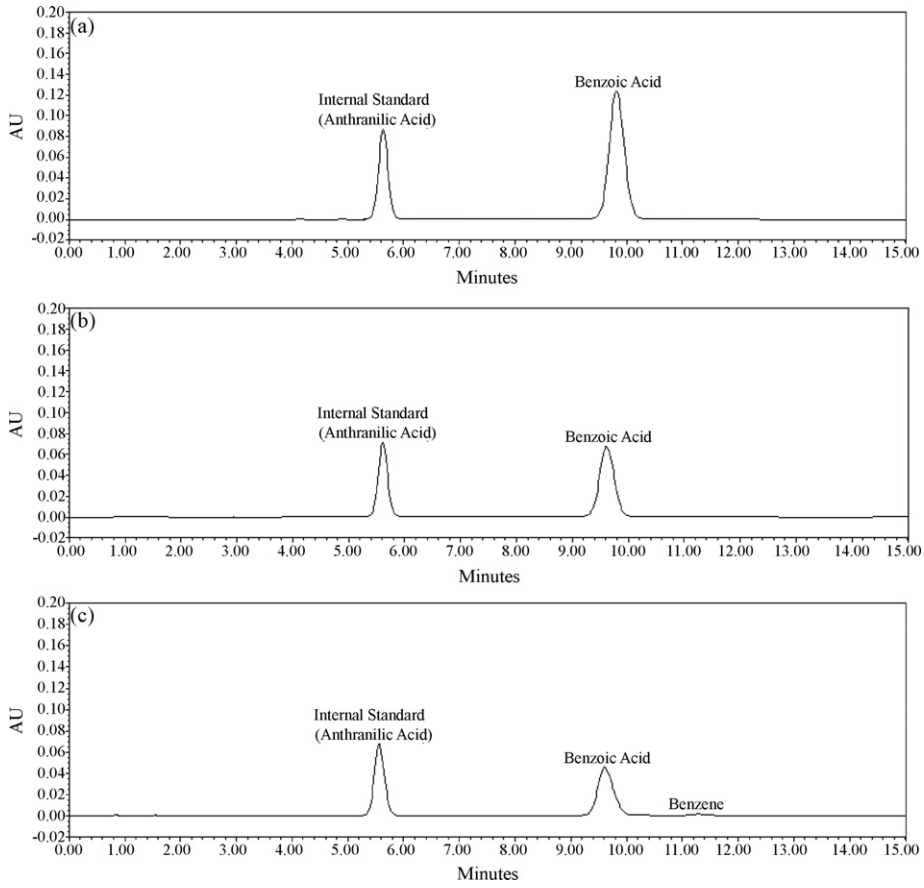

Fig. 6. HPLC chromatograms of the benzoic acid–water mixture after heating at 350 °C for (a) 30 min, (b) 150 min, and (c) 630 min.

As shown in Fig. 7, the main degradation product of each acid is the result of the loss of carbon dioxide from each acid. In other words, the carboxyl group in each acid was replaced by the hydrogen originally attached to the carboxyl group.

Chuchev and BelBruno proposed reaction mechanisms for the decarboxylation of *ortho*-substituted benzoic acids under neutral conditions [46]. Their computational studies of anthranilic acid involved a water molecule bridging the hydroxyl and amino groups to create a transition state. As shown in Fig. 8, the reaction begins with a lengthening of the carboxyl carbon–carbon distance, follows by migration of the carboxyl hydrogen to the water, and ends with a transfer of the water hydrogen to the benzene ring, which results in the loss of carbon dioxide. This is considered as the decarboxylation mechanism [46].

The decarboxylation reactions obtained from our experiments agree with this computational reaction model. The amino, hydroxyl, and methoxy groups of anthranilic acid, salicylic acid, and syringic acid are activating groups. These activating groups facilitate the thermal decarboxylation of the carboxyl group for each benzoic acid derivative causing the degradation in subcritical water. Benzoic acid lacks an activating group which may account for its exceptional stability.

To further understand the degradation of benzoic acid and derivatives in subcritical water, quantification of the degradation products was determined by HPLC analysis. The percent yield of each degradation product was calculated based on both stoichiometry according to the degradation reactions depicted in Fig. 7 and the HPLC analysis. The comparison of the percent degradation of benzoic acid derivatives and the percent yield of each degradant is given in Table 1. It is clear that for each acid the percent yield of the degradant is correlated with the percent degradation of the

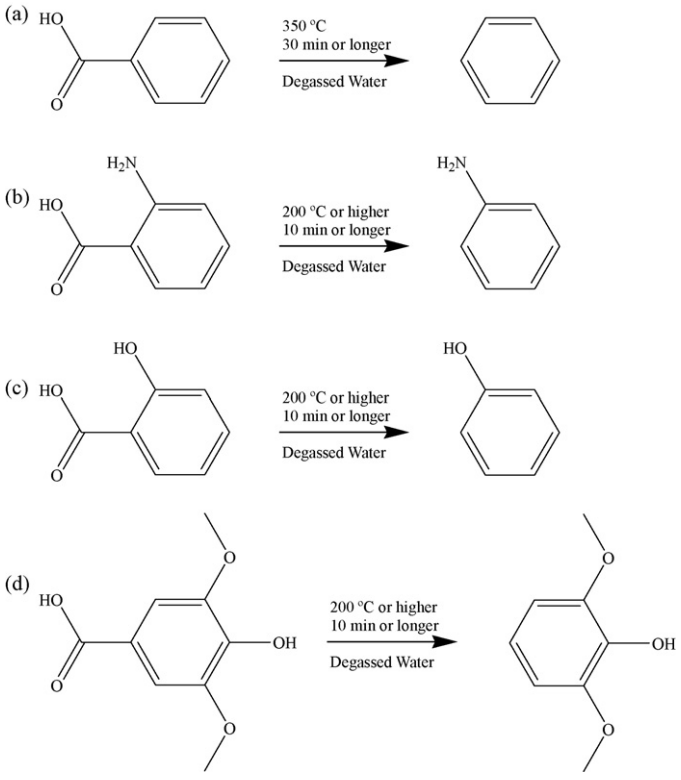

Fig. 7. Degradation reactions of benzoic acid and derivatives: (a) benzoic acid; (b) anthranilic acid; (c) salicylic acid; and (d) syringic acid.

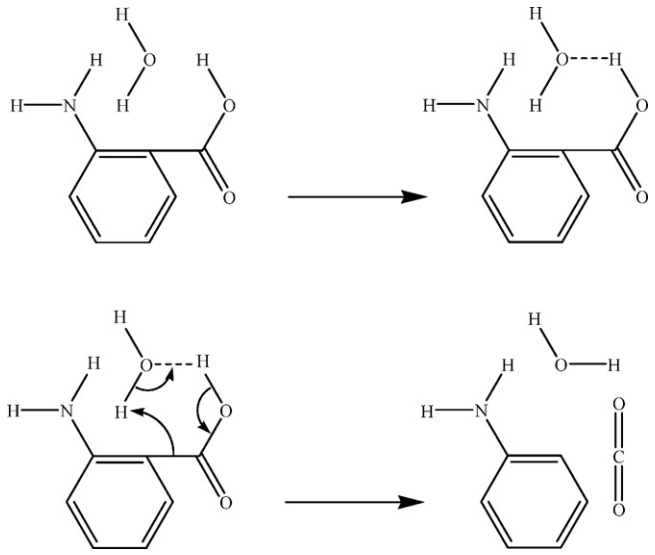

Fig. 8. Decarboxylation mechanism for anthranilic acid [46].

acid. When acid degradation was intensified at 250 °C compared to that at 200 °C, the degradant yield was also increased at the higher temperature. This is true for all three acids listed in Table 1.

Based on the 1:1 (acid:degradant) stoichiometry for the degradation reactions shown in Fig. 7, the percent yield of the degradant should equal the percent degradation of the acid if there is only one degradation product for each acid. The data in Table 1 indicate that phenol is the only degradation product for salicylic acid since the percent degradation of salicylic acid is similar to the percent yield of phenol. Although, the % yield is higher than the % degradation at 200 °C, the quantification of both degradation and yield can be considered as similar considering the relative standard deviation of the two values as shown in Table 1. It should be pointed out that the data for salicylic acid and phenol shown in Table 1 indicate no degradation of phenol in subcritical water at 200 and 250 °C. Our previous study shows that phenol is stable in water at temperatures up to 250 °C [47].

Please note that the percent yield is lower than the percent degradation for both anthranilic and syringic acids as reported in Table 1. There are two possibilities for the lower percent yield values. First, there might be other degradation products. The other possibility might be the degradation of the degradants in subcritical water causing the lower percent yield. Because the acid degradation mechanism is the same for all four acids studied and only one degradation product (phenol) was obtained from salicylic acid degradation as discussed earlier, we tend to believe that degradation of the degradants in subcritical water is the reason for the lower yield of the degradation products.

Table 1
Comparison of the degradation of benzoic acid derivatives and the yield of their degradation products after heating at 200 and 250 °C for 30 min.

Benzoic acid derivatives	% Degradation (% RSD[a])	Degradants	% Yield (% RSD[a])
Anthranilic acid, 200 °C	91 (4.9)	Aniline	73 (35)
Anthranilic acid, 250 °C	100 (0.1)	Aniline	81 (11)
Salicylic acid, 200 °C	69 (6.7)	Phenol	78 (12)
Salicylic acid, 250 °C	98 (1.5)	Phenol	97 (5.5)
Syringic acid, 200 °C	44 (14)	Syringol	41 (5.6)
Syringic acid, 250 °C	99 (0.1)	Syringol	67 (7.5)

[a] Based on triplicate measurements.

The percent yield of benzene, the degradation product of benzoic acid, is shown in Fig. 6. Again, there is a good correlation between benzoic acid degradation and benzene formation.

4. Conclusions

All four acids investigated remained stable in water at temperatures up to 100 °C. The three benzoic acid derivatives showed very mild degradation after heating in water at 150 °C for 30 min. Severe degradation of benzoic acid derivatives was observed at 200 °C while their complete degradation occurred at 250 °C. However, benzoic acid remained stable at temperatures up to 300 °C after heating for 10 min. The degradation products of each acid were identified and quantified by HPLC and further confirmed by GC/MS. Under subcritical water conditions anthranilic acid, salicylic acid, syringic acid, and benzoic acid undergo decarboxylation to form aniline, phenol, syringol, and benzene, respectively. The percent degradation of benzoic acid and its derivatives is in good correlation with the percent yield of their degradation products.

Acknowledgements

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