Oxidation of Dicarboxylic Acids in Supercritical Water

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(Received December 16, 2002; CL-021064)

Sebacic and azelaic acids were oxidized in a batch reactor at 400 °C to study the oxidation pathways and mechanisms of dicarboxylic acids in supercritical water. The reaction of dicarboxylic acids proceeds with the consecutive oxidation of higher to lower molecular weight dicarboxylic acids through α-, β- and γ-oxidations, as do monocarboxylic acids. The oxidation of dicarboxylic acids is also accompanied by decarboxylation, leading to the formation of monocarboxylic acids. Decarboxylation occurred only when some oxygen was supplied.

Our previous studies on supercritical water oxidation (SCWO) of garbage[1,2] and lignocellulosic wastes[3] have shown that the oxidation occurs via carboxylic acids and most of the reaction time for their destructive oxidation is used for oxidation of carboxylic acids.

SCWO of high molecular weight monocarboxylic acids has shown that the oxidation occurs not only at the carbons in the α-, β- and γ-positions to a COOH group, but also at the carbon in the β-position to the methyl group ((ω-1)-carbon).[4] The (ω-1)-oxidation may lead to the formation of dicarboxylic acids and many dicarboxylic acids have been detected as intermediate products in the oxidation of monocarboxylic acids. However, the oxidation of dicarboxylic acids in supercritical water remains poorly understood.

In this study, sebacic acid ($HOOC(CH_2)_8COOH$) and azelaic acid ($HOOC(CH_2)_7COOH$) were used as the test materials. All experiments were performed with a batch reactor made of SUS 316 with an internal volume of 5.7 cm^3. The experimental setup has been described in detail elsewhere,[2] and only a brief description is given below. A 0.07 g test material and H_2O_2-water mixture of 1.71 cm^3 in volume were added to the batch reactor, and then the reactor was put into a salt bath preheated to 400 °C. The reaction pressure was 25–33 MPa. After 30 s, the reactor was removed from the salt bath and put into a cold water bath to quench the reaction. Liquid samples were taken out of the reactor by washing with CH_3OH for analyses by GC/MS, HPLC, and ^{1}H-NMR. In order to detect as many intermediate oxidation products as possible, oxygen supply was changed in the range of insufficient oxygen supply. A 100% oxygen supply is defined as the stoichiometric demand of oxygen for complete oxidation of the test material to CO_2 and H_2O.

Figure 1 shows the variation of GC/MS total ion chromatograms of samples for the oxidation of sebacic acid with an oxygen supply. Many peaks appeared, which were identified by the total and selected ion chromatograms with the aid of a computer library, as well as the GC retention times of the products and authentic compounds. Dicarboxylic acids with 4–10 carbon atoms are identified. Dicarboxylic acids with 2–3 carbon atoms were detected by HPLC (data not shown). Therefore, all dicarboxylic acids below 10 carbon atoms were identified. It should be noted that although peak areas of dicarboxylic acids in Figure 1 seem to be small, their amounts are not so small, because these dicarboxylic acids have high boiling points. Figure 2 gives expanded chromatograms at 33–55 min for Figure 1. It is understandable that peaks of high molecular weight dicarboxylic acids become small, and in contrast, the peaks of low molecular weight carboxylic acids gradually become larger with an increase in the oxygen supply. These results may suggest that the reaction of dicarboxylic acids proceeds with the consecutive oxidation of higher molecular weight carboxylic acids to lower molecular weight carboxylic acids. In addition, from Figure 1, monocar-

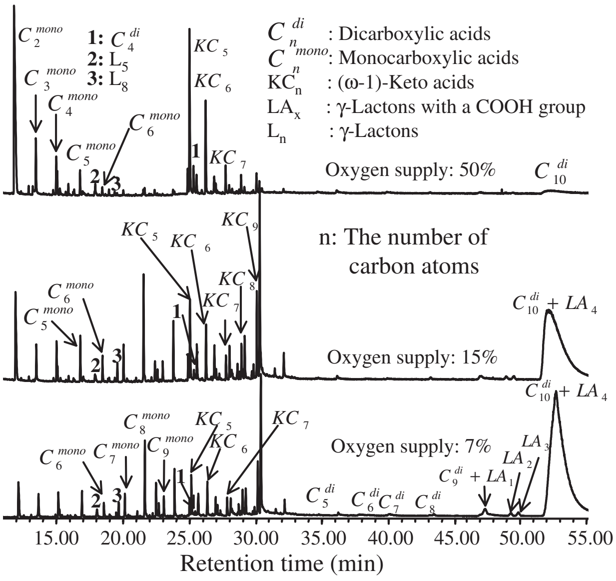

Figure 1. Variation of GC/MS chromatograms of intermediate products for the oxidation of sebacic acid with oxygen supply.

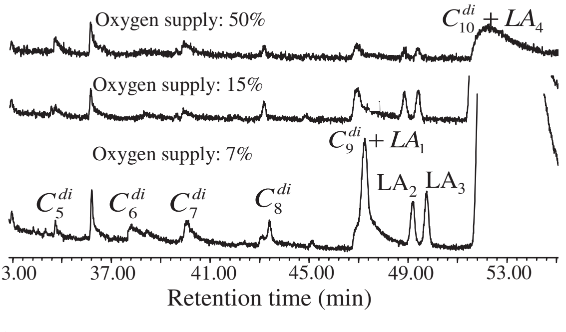

Figure 2. Expanded chromatograms at 33-55 min for Figure 1.

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boxylic acids of C_{1-9}^{mono} were also identified. Similar results were also obtained for the experiment with azelaic acid C_9^{di}. Note that the amounts of monocarboxylic acids are very small, although their peaks seem to be larger than those for dicarboxylic acids.

For the formation of dicarboxylic acids, a possible mechanism may be explained as the reaction proceeding with the consecutive oxidation of a higher molecular weight dicarboxylic acid to a lower molecular weight dicarboxylic acid through α-, β- or γ-oxidation, as do monocarboxylic acids.[4] Identification of C_9^{di} for the oxidation of C_{10}^{di}, and C_8^{di} for C_9^{di} supports the presence of α-oxidation, because α-oxidation should give a carboxylic acid with one less carbon atom, as reported in a previous study on monocarboxylic acid oxidation.[4]

It can be also seen that from Figure 1, the peaks of (ω-1)-keto acids with carbon numbers of 5–9 were found. The formation of (ω-1)-keto acids indicates the presence of β-oxidation, whose possible pathway is that a hydroperoxide, $HOOC–(CH_2)_{n-2}–C(OOH)–CH_2–COOH$, is first formed by the β-hydrogen abstraction by a hydroxyl radical, and then the hydroperoxide undergoes decomposition, yielding a β-keto dicarboxylic acid. The β-keto acid is decarboxylated easily and yields a (ω-1)-keto monocarboxylic acid. Further oxidation of (ω-1)-keto monocarboxylic acid would lead to the formation of dicarboxylic acids through the oxidation at α-, β- or γ-carbon either to the CO or COOH group, where diketones would be a characteristic intermediate product. In order to test this mechanism, an experiment with 7-oxo-octanoic acid was performed with a 7% oxygen supply. As shown in Figure 3, many dicarboxylic acids including C_7^{di} and some diketones like 2,5-hexanedione were identified. Note that monocarboxylic acids were also found.

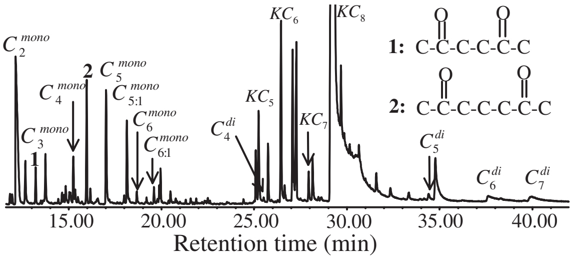

Figure 3. GC/MS chromatogram for the oxidation products of 7-oxo-octanoic acid with 7% oxygen supply.

Further, there is a group of peaks of $LA_1–LA_4$ in Figure 2. Note that LA_1 and C_9^{di}, LA_4 and C_{10}^{di} were not separated in Figure 2, but they were separated well in an extracted sample with dichloromethane. They were identified as γ-lactones bearing a carboxylic group attached to an alkane. The formation of γ-lactones bearing a carboxylic group provides the support of the presence of γ-oxidation, a possible mechanism for which is similar to that for monocarboxylic acids. That is, first, the attack at a γ-carbon by a hydroxyl radical yields a γ-hydroxy acid, which then loses water to yield a γ-lactone with a carboxylic group, because a γ-hydroxy acid easily loses water spontaneously to yield a γ-lactone.

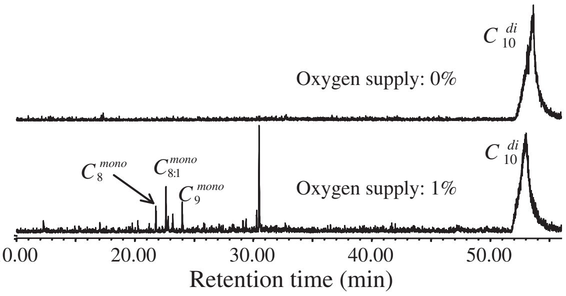

Figure 4. GC/MS chromatogram for the oxidation products of sebacic acid with 0% and 1% oxygen supply.

For the formation of monocarboxylic acids, it may be because the decarboxylation of dicarboxylic acids leads to the formation of monocarboxylic acids. Emanuel et al.[5] proposed that decarboxylation occurred in wet oxidation, that is, the oxidation in subcritical water, of monocarboxylic acids by a free-radical mechanism which did work only when oxygen was supplied: $ROO\cdot + RCOOH \rightarrow ROOH + RCOO\cdot$, $RCOO\cdot \rightarrow R\cdot + CO_2$. In order to test the decarboxylation mechanism of dicarboxylic acids in supercritical water, experiments using C_{10}^{di} without oxygen supply and with 1, 2 or 5% oxygen supply were performed. As shown in Figure 4, monocarboxylic acids were not found in the case without oxygen supply, but were formed in the cases with oxygen supply. This result implies that the free-radical decarboxylation mechanism may work for dicarboxylic acids in supercritical water and suggests that the oxidation of dicarboxylic acids is accompanied by the decarboxylation which leads to the formation of monocarboxylic acids, although the amounts of monocarboxylic acids found were very small.

According to this mechanism, C_9^{mono} should come from only the decarboxylation of C_{10}^{di} for the oxidation of C_{10}^{di}, while C_{2-8}^{mono} can be from not only the decarboxylation of dicarboxylic acids but also from further oxidation of the monocarboxylic acids formed, because the oxidation of monocarboxylic acids proceeds mainly with the consecutive oxidation of higher to lower molecular weight monocarboxylic acids.[4] These discussions may lead to the conclusion that the reaction rate of decarboxylation is much lower than that of consecutive oxidation of dicarboxylic acids.

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