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KINETICS, CATALYSIS, AND REACTION ENGINEERING

Kinetics and Mechanism of Wet Air Oxidation of Butyric Acid

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Low molecular weight acids are common intermediate reaction compounds formed during the wet air oxidation (WAO) of aqueous waste streams, and frequently their oxidation is the rate-controlling step in the overall reaction. The WAO kinetics of aqueous solutions of butyric acid was studied in a stainless steel 316 autoclave over a temperature range of 200−320 °C with a total pressure of 15 MPa of synthetic air, which provides an excess of oxygen. Kinetic models were developed with respect to various concentrations of butyric acid and chemical oxygen demand (COD). Oxidation reactions always obeyed a pseudo-first-order kinetic, but two different activation energies were needed to represent the temperature dependence in two ranges, namely 200−275 and 275−320 °C. This finding can be explained by the competition between two main reaction pathways in the oxidation of the acid, since both pathways take place simultaneously. A mechanism in accordance with the results obtained is proposed.

1. Introduction

Wet air oxidation (WAO), which is also known as subcritical hydrothermal oxidation, is an attractive treatment for waste streams that are too dilute for incineration and too concentrated or toxic for biological treatment.[1] This process can be defined as the oxidation of organic and inorganic substances, in an aqueous solution or suspension, by means of oxygen or air at elevated temperatures (150−320 °C) and pressures (0.5−20 MPa). The enhanced solubility of oxygen in aqueous solutions at elevated temperatures and pressures provides a strong driving force for oxidation. WAO has been tested on both pure components and real wastewaters, producing effluents that contain water, CO_2, and other innocuous intermediates and end products. To study the kinetics involved and to understand better the WAO process, numerous model compounds have been tested, either because they are present in many industrial wastewaters or because they are intermediates formed during the process.[2] The oxidation of low molecular mass acids has received the most attention since they are refractory in nature and they appear as the ultimate intermediates in oxidation pathways of most organic pollutants. Acetic acid has been found to be a major intermediate that is relatively difficult to remove under wet oxidation conditions, and thus has been the subject of several studies.[3−5] Propionic acid is the second-most refractory compound and has also been studied by several authors.[6−9] Butyric acid is also very refractory to WAO; however, relatively few studies have been reported in the literature for butyric acid oxidation.[8,10] A number of studies on formic acid,[3−5] oxalic acid,[5,11,12] glioxalic acid,[5,12] and other low mass carboxylic acids can also be found in the literature.[11,13] The kinetic parameters reported by these previous studies are summarized in Table 1. Although many kinetic studies have been carried out, little clear information on the reaction mechanism has been presented even for simple model compounds.

Butyric acid is one of the most important intermediate products of the thermal decomposition of several types of industrial wastewater,[14] and it has been found as a common intermediate formed in the oxidation of long chain carboxylic acids.[15] In this work, WAO of butyric acid has been studied at different temperatures to obtain the kinetics of this refractory compound, and a reaction mechanism based on two main pathways is proposed to explain the kinetic results obtained.

2. Experimental Apparatus and Procedure

2.1. Materials. Butyric acid (C4, minimum 99%) was supplied by Sigma and used without further purification. Concentrated aqueous solutions were prepared prior to injection into the reactor. Ten milliliter samples of concentrated solutions, with a concentration of around 15 g/L, were injected into the reactor to give an initial concentration of around 1 g/L butyric acid at the beginning of each experiment.

Synthetic air (Carburos Metálicos, 99.99% pure) was used as oxidant and was obtained from a synthetic air cylinder connected to the reactor.

2.2. Equipment. Figure 1 shows a schematic drawing of the apparatus used in this work. WAO experiments were carried out in a 316 stainless steel reactor (Autoclave Engineers) with a capacity of 300 mL. The vessel was fitted with a variable-speed stirrer (MagneDrive) and an electric heater. A constant temperature was maintained at ±2 °C from the set point by means of an electronic controller (PID). The experimental system incorporated a rupture disk with a burst pressure of 20 MPa as a safety device in case of pressure buildup in the reactor during the experiment.

The aqueous solution of butyric acid was placed in the injector, which consisted of a tube (0.61 cm i.d., 0.95 cm o.d.) with a volume of 10 mL. The sampling port for drawing off liquid samples consisted of tubing (0.14 cm i.d., 0.32 cm o.d.)

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Table 1. Kinetic Parameters for Noncatalytic WAO of Selected Carboxylic Acids

acid	init concn (g/L)	reactor type and material	temp (°C)	oxygen press. (MPa)	preexponential factor[a]	activation energy (kJ/mol)	acid order, *m*	oxygen order, *n*	ref(s)
formic acid, HCOOH	24−43	batch, SS-316	190−313	2.0−20	3.10×10^{9}	143.5	1.33	0.46	3
formic acid, HCOOH	3.83	batch, SS-316	150−240	0.35−1.38	4.71×10^{10}	121.3	1.00	0.86	4
acetic acid, CH_3COOH	30	batch, SS-316	270−320	2.0−20	5.60×10^{10}	167.7	1.00	0.37	3
acetic acid, CH_3COOH	1.0	batch, titanium	150−320	2.5−5.5	7.59×10^{10}	177.7	1.00	0.5	5
propionic acid, CH_3CH_2COOH	1.0	batch, titanium	280−310	1.0−4.5	2.65×10^{10}	150.6	1.00	0.5	6
propionic acid, CH_3CH_2COOH	7.4−14.8	batch, SS-316	232−288	1.7−5.2	9.32×10^{12}	135	1.43	0.39	7, 8
propionic acid, CH_3CH_2COOH		batch, SS-316	250−275			139	1.00	0.00	9
3-hydroxypropionic acid, CH_2OHCH_2COOH	1.0	batch, titanium	280−310	1.0−4.5	1.73×10^{9}	135.4	1.00	0.5	6
oxalic acid, COOHCOOH	1.2[b]	batch, SS-316	225−245	0.7−1.0	1.26×10^{9}	129.4	1.00	0.32	12
oxalic acid, COOHCOOH	0.1−0.2	batch, SS-316	227−288	2.0−20	6.83×10^{8}	133.8	1.00	0.31	11
oxalic acid, COOHCOOH	0.5	batch, titanium	150−320	0.8−6	1.31×10^{11}	137	1.00	0.50	5
glyoxalic acid, CHOHCOOH	1.0−2.5	batch, SS-316	150−200	0.35−1.38	1.45×10^{5} [c] 2.87×10^{9} [d]	53.5[c] 117[d]	1.00[c] 1.00[d]	0.92[c] 0.20[d]	12
glyoxalic acid, CHOHCOOH	1.0	batch, titanium	150−320	0.8−6.0	2.25×10^{9}	97.4	1.00	1.00	5
acrylic acid, $CH_2CHCOOH$	0.5	batch, titanium	180−280	1.0−5.5	1.08×10^{6}	94.4	1.50	0.05	14
maleic acid, $COOH(CH)_2COOH$	0.3	batch, titanium	180−280	1.0−5.5	3.68×10^{7}	99.9	1.45	0.12	14
fumaric acid, $COOH(CH)_2COOH$	0.3	batch, titanium	180−280	1.0−5.5	8.91×10^{5}	83.6	1.45	0.54	14
butyric acid, $CH_3(CH_2)_2COOH$	8.8−17.6	batch, SS-316	238−257	6.8−13.6	1.26×10^{9}	29.7	1.40	0.46	10
butyric acid, $CH_3(CH_2)_2$ COOH	1.0	batch, SS-316	200−275	15	1.49	44.8	1.00	0.00	this work
butyric acid, $CH_3(CH_2)_2COOH$	1.0	batch, SS-316	275−325	15	8.38×10^{9}	146.9	1.00	0.00	this work

[a] L^{m+n-1} mol^{1-m-n} s^{-1}. [b] Based on COD. [c] First step. [d] Second step.

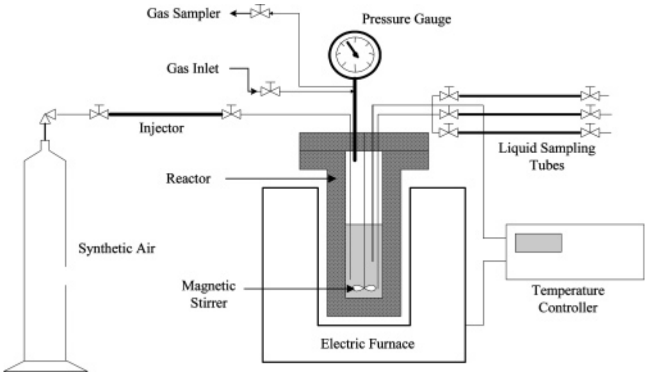

Figure 1. Schematic diagram of the wet air oxidation reactor system.

running from the top of the reactor to the bottom, connected to three external sampling tubes (0.46 cm i.d., 0.64 cm o.d.), each with a volume of 7 mL. This sampling system was specially designed by our group to enable several samples to be drawn off over a short time interval.[15]

2.3. Procedure. The operating procedure for the WAO experiments was as follows: 150 mL of deionized water and a calculated amount of synthetic air were introduced into the reactor. The reactor was then heated to the temperature set point and the stirrer speed was set to 14 rev/s. In a previous study we confirmed that, when the stirrer speed was set at 10 rev/s or more, the resistance of the mass transfer of oxygen from the gas phase to the liquid phase was eliminated.[16] Once the desired temperature had been reached, the concentrated solution of butyric acid was placed in the injector, without preheating, and was then injected into the reactor by means of the pressure supplied by the bottled compressed air; in this way, the reaction pressure was maintained at 15 MPa (this involves an oxygen excess, always more than 7 times the stoichiometric amount needed to oxidize the butyric acid completely). The time of injection was taken as time zero for the reaction, and liquid samples were periodically withdrawn and analyzed. The small volume injected did not produce significant fluctuation of the temperature from its set point during sample injection. The operating pressure was maintained at ±1 MPa during the experiments by supplying new compressed air from the bottle. Further details of the apparatus and procedure can be found in a previous publication.[15]

2.4. Analytical Methods. An HP 6890 Series gas chromatograph, fitted with an flame ionization detector (FID), was used to analyze the concentration of butyric acid and to monitor the formation of intermediates and final products. A Nukol column was employed (Supelco) (15 m × 0.53 mm i.d., 0.50 μm film thickness). The efficiency of the oxidation process was also monitored in terms of the reduction in chemical oxygen demand (COD). The COD measurements were obtained according to the dichromate standard method.[17] All possible reaction intermediates were analyzed by GC/MS using Voyager equipment (Thermo Quest) including a gas chromatograph 8000 TOP and a Fison mass spectrophotometer of low resolution. A 30 m semipolar capillary column (Dbwax, Supelco) and splitless injection were used, and the compound assignment was made by using the NIST library. Gas samples were analyzed using an HP 6890 PLUS gas chromatograph with a thermal conductivity detector (TCD). Two in-series columns were used to separate CO from CO_2: the first column was a Porapack-Q column and the second was a molecular sieve Carvosieve column (Supelco).

3. Results and Discussion

As shown in Figure 2, the efficiency of both butyric acid and COD removal by WAO is highly influenced by the temperature. The use of 275 °C for 120 min results in a very low reduction of the butyric acid concentration (<40%), thus confirming the refractory character of this acid at mild conditions. It is necessary to operate at temperatures over 300 °C and reaction times of at least 90 min to remove 80% of the butyric acid present in the solution. The temperature effect on the reaction rate is widely known, but in this case we can observe two ranges with a different dependence versus temperature (this fact will be demonstrated in Figure 4, where an Arrhenius representation is shown). At low temperatures (200−275 °C), an increase of 50 °C does not enhance the butyric acid removal to any significant extent. However, at temperatures above 275 °C a significant increase in the butyric acid oxidation is observed versus temperature. This could be explained by a change in the pathway followed for the oxida-

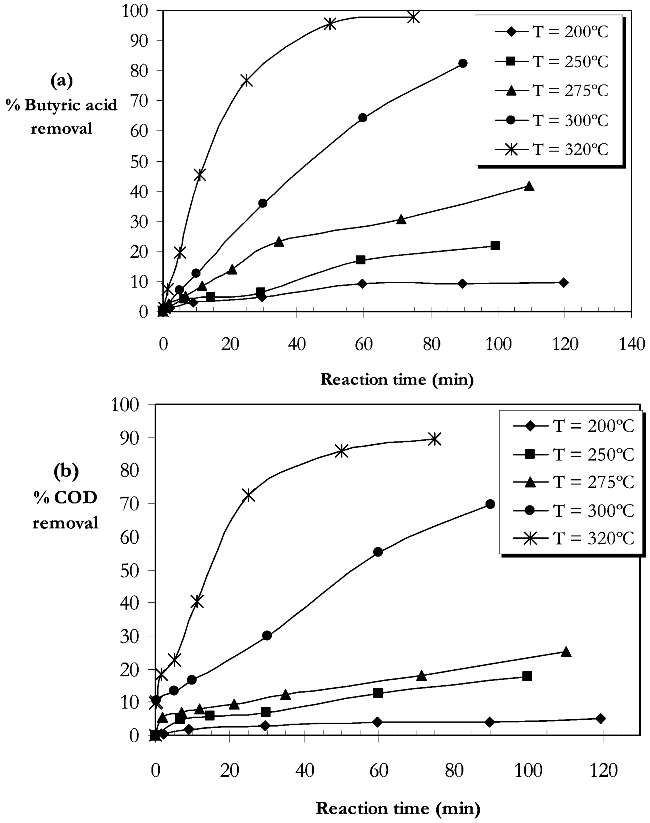

Figure 2. Effect of temperature on the removal of butyric acid (a) and COD (b) (total pressure 15 MPa).

tion of that acid. In both pathways there is an Arrhenius behavior, but to a different degree. This hypothesis will be detailed later.

The results obtained show that COD removal curves have an evolution similar to butyric acid removal in the oxidation process (Figure 2b). However, a lower degree of elimination is observed in every case for COD removal, due to the persistence of intermediate oxidation products that contribute to COD, such as acetic, propionic, and other organic acids that are refractory to wet air oxidation. This finding reflects the resistance of this acid to complete oxidation under the conditions studied.

3.1. Kinetics of WAO Based on Butyric Acid and COD Removal. The initial oxygen concentration is much greater than the initial butyric concentration (in all experiments over 7 times the stoichiometric amount needed to oxidize the butyric acid completely), so oxygen concentration can be considered as practically invariable during the reaction, and it is possible to approximate the kinetic expression to pseudo first order, given by eqs 1 and 2 for butyric acid and COD, respectively:

$$-\ln\frac{C_{\mathrm{BA}}}{C_{\mathrm{BA}_0}} = kt \qquad (1)$$

$$-\ln\frac{C_{\mathrm{COD}}}{C_{\mathrm{COD}_0}} = kt \qquad (2)$$

where C_{BA} is butyric acid concentration (mg/L), C_{COD} is concentration of organic compounds expressed as chemical oxygen demand (mg of O_2/L), t is reaction time (min), and k is the pseudo-first-order rate constant (min^{-1}). Subscript "0" denotes "initial".

Thus, the rate constant can be calculated from the slope of the straight line obtained when $\ln C/C_0$ is plotted against time.

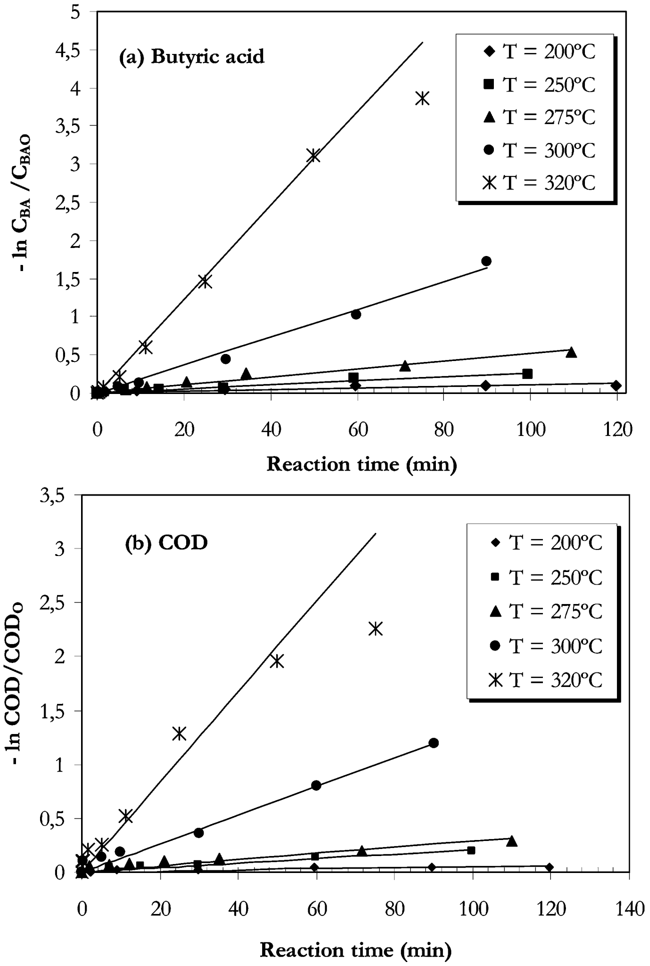

Figure 3. Pseudo-first-order kinetics plot for butyric acid (a) and COD (b).

Figure 3 shows the results of the linear regression for experimental data for butyric acid and COD reduction, respectively.

Assuming an Arrhenius dependence of temperature, k can be expressed as

$$k = A\exp\left(-\frac{E_{\mathrm{a}}}{RT}\right) \qquad (3)$$

where A is the preexponential factor (s^{-1}), E_{a} is the apparent activation energy (kJ/mol), R is the universal gas constant (8.314 J mol^{-1} K^{-1}), and T is the temperature (K).

The Arrhenius plot showing $\ln k$ versus $1/T$ is shown in Figure 4. Similar results are obtained for both butyric acid concentration and COD removal, but the values of k are slightly lower for COD since its removal depends on intermediate product oxidation, such simple organic acids, which present great resistance to oxidation. The Arrhenius parameters obtained in this work for butyric acid are presented in Table 1. As can be seen, there are two different temperature dependences in the range studied. In the range of 200−275 °C, a low value of the activation energy (45 kJ/mol) shows that the reaction rate is slightly enhanced by a small increase of temperature. However, in the range of 275−320 °C the reaction rate is strongly influenced by temperature, showing a considerably higher value for the activation energy (147 kJ/mol). If all data were fitted with a unique linear regression, the activation energy would be 81.6 kJ/mol (r^2 = 0.889), in clear disagreement with the activation energy found by Williams et al.[8] for WAO of butyric

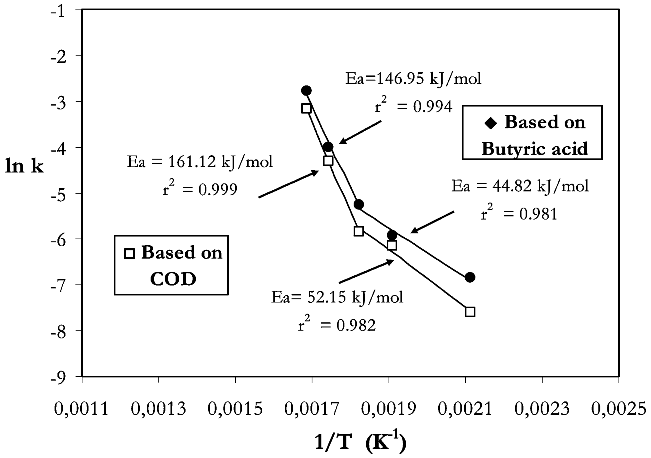

Figure 4. Arrhenius plot for pseudo-first-order rate constants calculated from both butyric acid and COD removal data.

acid (29.7 kJ/mol), since they worked in the range of lower temperatures (namely 238−257 °C).

Based on experimental findings, the rate equation (mol L^{-1} s^{-1}) for WAO of butyric acid is given by two different equations depending on the range of temperatures used:

$$\text{for } 200-275\ ^\circ\text{C} \qquad r_{BA} = 1.49 \exp[-44820/RT][BA] \quad (4)$$

$$\text{for } 275-320\ ^\circ\text{C} \qquad r_{BA} = 8.38 \times 10^9 \exp[-146900/RT][BA] \quad (5)$$

Based on COD measurements

$$\text{for } 200-275\ ^\circ\text{C} \qquad r_{COD} = 4.90 \exp[-52150/RT][COD] \quad (6)$$

$$\text{for } 275-320\ ^\circ\text{C} \qquad r_{COD} = 1.075 \times 10^{11} \exp[-161100/RT][COD] \quad (7)$$

Similar results can be found in the literature in other Arrhenius plots, for example in the WAO of glyoxalic acid,[5] oxalic acid,[12] and propionic and hydroxypropionic acids,[6] where it is possible to distinguish to different behaviors at different temperatures. Nevertheless, authors usually ignore the existence of two different temperature dependences by fitting all data (in most cases only three temperatures studied) with a single linear regression, assuming that the lack of linearity observed is due to experimental errors.

That fact could be one of the reasons why there is a notable lack of agreement among the kinetic parameters published by different authors, as was demonstrated in an earlier study that compared all the studies of hydrothermal oxidation of phenol.[18] It is important to point out that, in all cases, the activation energy obtained is not the intrinsic one and it can only be considered as a parameter that predicts the temperature dependence of the acid disappearance rate in the range studied. Moreover, kinetic parameters obtained have an element of uncertainty associated with them, and must be used with caution.

To validate the findings of this work, Figure 5 shows a parity plot for experimental conversions and those conversions predicted by the kinetic parameters obtained based on butyric acid and those based on COD. In both cases, the predictions made by using the corresponding Arrhenius parameters for each temperature range are quite satisfactory. Since the different trends in the Arrhenius plot are very clear, a mechanism according to the results obtained is proposed in this work.

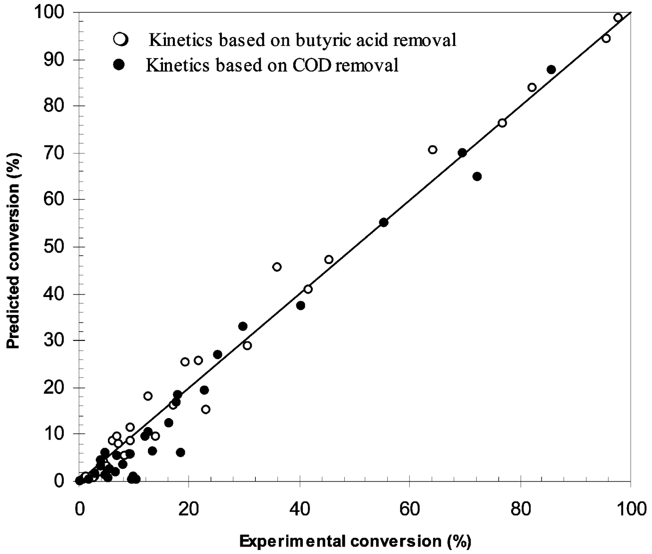

Figure 5. Comparison between experimental conversions and those predicted by kinetic parameters obtained.

3.2. Reaction Pathways. According to the mechanisms described by Sève and Antonini,[19] numerous intermediates can be formed during the wet oxidation of saturated fatty acids. Radicals R• are formed the most rapidly, and a hydroperoxide (ROOH) would be formed on the α-carbon. The hydroperoxide will decompose into alkoxyl (RO•) and hydroxyl radicals (OH•). This RO• may follow two pathways:

(a) The first pathway produces CO_2 and an aldehyde that is then oxidized to the corresponding acid (this acid will repeat the process to produce a new carboxylic acid of $n - 1$ atoms).

(b) The second produces glyoxylic acid (that may be oxidized to oxalic acid) and a $n - 1$ carbon atom alcohol, aldehyde, or carboxylic acid that will follow a pathway similar to (a).

According to these authors, in the case of a saturated fatty acid of n carbon atoms, the reaction mechanisms involve the formation of carboxylic acids from $n = 2$ to $n - 1$ carbon atoms as well as the corresponding aldehydes, glyoxylic acid, and oxalic acid.

Based on our findings, we assume that pathway b is not likely to occur in the case of WAO of butyric acid, since none of our samples contained either glyoxylic acid or oxalic acid. Besides, acetone was found in all samples and its generation is not predicted by any of the pathways proposed by those authors.

According to the mechanism proposed by Williams et al.[10] for the oxidation of butyric acid, besides the formation of an α-hydroxy acid, the β-carbon can also be attacked to form a β-hydroxy acid that will be subsequently oxidized to form acetone and CO_2. Based on our results, this second pathway takes place simultaneously at all temperatures since we have detected the formation of acetone in all the experiments carried out in this study. Those authors show the formation of several aldehydes and alcohols in the mechanism, but we will not include them in this work because in the presence of an oxidant they are very rapidly oxidized to the corresponding acids and they are not likely to be present in the samples. That is the case of acetaldehyde, which would only be present in the liquid samples under conditions of oxygen deficiency. When an oxidant is present, the route leading to the formation of acetic acid predominates. It is important to point out that the real reaction mechanism is much more complex and a huge amount of unstable intermediates can be formed. As an example, Dagaut et al.[20] proposed more than 100 elementary reactions to describe the hydrothermal oxidation of methanol.

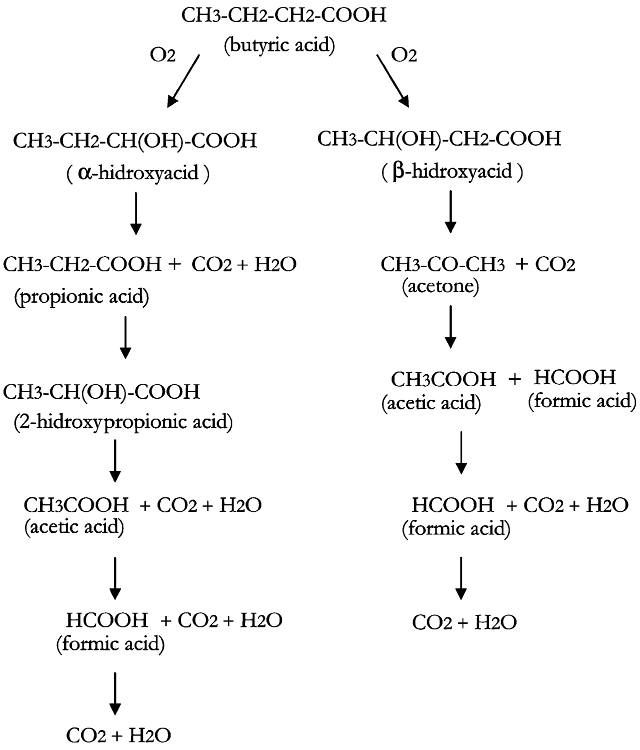

Figure 6. Simplified reaction pathways proposed for WAO for butyric acid.

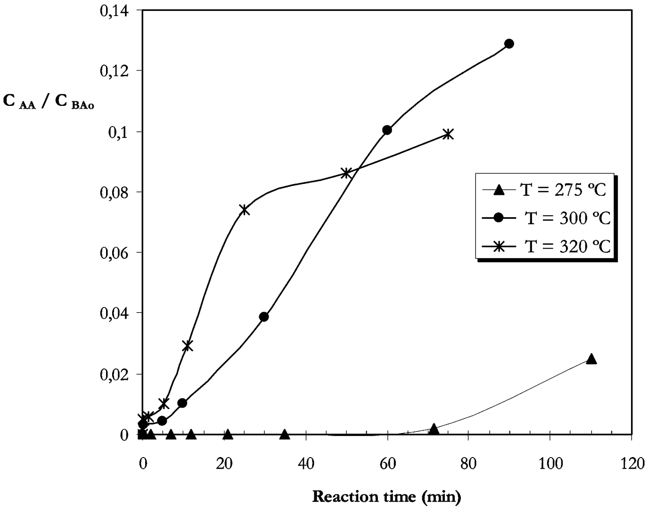

Figure 7. Formation of acetic acid at different temperatures. Acetic acid concentrations (C_{AA}) have been normalized by the initial concentration of butyric acid (C_{BA_0}).

Figure 6 shows the simplified oxidation pathways for WAO of butyric acid proposed in this work. The oxidation on the α-carbon produces CO_2 and the $n - 1$ carbon corresponding acid (namely propionic acid, which will repeat the process to produce acetic acid). At temperatures below 275 °C, a small amount of butyric acid is oxidized to propionic acid, but no further oxidation follows. This fact can be demonstrated because at temperatures ≤275 °C we found carbon dioxide in the gas phase, but no acetic acid was found in the liquid phase. At 300 °C, both propionic and acetic acids are present in the liquid samples. At 320 °C, propionic acid is fully oxidized and only acetic acid is detected in the liquid. Figure 7 shows the amount of acetic acid formed at different temperatures and reaction times. These findings are in agreement with the results of Shende and Levec,[6] who studied the wet oxidation of propionic acid at temperatures up to 310 °C. As suggested in the literature,[21] the *β*-carbon can also be attacked to produce CO_2 and acetone. Although this second pathway is supposed to be less favored, the presence of acetone in all samples must be explained by its stability at the conditions studied, where it is not further oxidized. The generation of those refractory intermediates explains the low conversions observed at temperatures below 275 °C (Figure 2). Further decomposition of acetic acid requires a relatively higher activation energy, and that is the reason why acetic acid is the major and stable WAO intermediate.[22] On the other hand, once formic acid is formed, it decomposes readily even at low temperatures and it was never detected in our liquid samples. As a general rule, the rate of decomposition increases by the number of carbon atoms as larger molecules decompose into smaller ones and CO_2. An exception is formic acid, the lower end member of the fatty acid series, which decomposes at a rate several times higher than that of the other compounds.[3]

These results, in combination with literature data, are the basis for the proposed pathways for hydrothermal reactions involving butyric acid. The competition between two main reaction pathways in the oxidation of butyric acid could explain the double temperature dependence found in this work, although both pathways take place simultaneously even at low temperatures. It is very likely that the reaction extent of each route can differ with the temperature. If we assume that both reactions are of first order and occur in parallel, the integral form of the kinetic equation is

$$C = C_0(\alpha e^{-k_1 t} + (1 - \alpha)e^{-k_2 t}) \qquad (8)$$

where α is the fraction of C_0 (initial concentration) that is oxidized by pathway 1 (k_1 being the first-order kinetic parameter) and $(1 - \alpha)$ is the fraction of substrate that reacts through pathway 2 (k_2 being the first-order kinetic parameter). If α is temperature dependent, then k_1 and k_2 may show more importance in the kinetics, being responsible for the experimental results, since k_1 and k_2 could have different Arrhenius parameters. A similar kinetic model based on two parallel reactions with different temperature dependences can be found in the literature.[23]

However, the change in the temperature dependence could also be explained by a change in the formation, stability, or reactivity of radicals. In the absence of promoters, the commonly accepted mechanism for the autoxidation of organics with oxygen starts with the following reaction:

$$RH + O_2 \rightarrow R\bullet + HO_2\bullet \qquad (9)$$

At high temperatures, reaction 9 is a viable source of radicals, but it is very slow at low temperatures, since ground-state oxygen does not react readily with most organic molecules because of its spin restrictions.[24] In this respect it is possible that below 275 °C the autoxidation mechanism is only effective in oxidizing a small amount of butyric acid but it is not capable of further oxidizing propionic acid or acetone. However, above 275 °C there must be a change in the reaction medium that is not well-known yet. It may concern the formation of other reactive radicals or peracids that would accelerate the subsequent reactions. These aspects need further research to understand better the chemistry of the process.

4. Conclusion

The WAO of butyric acid was found to follow pseudo-first-order kinetics in the range of operating conditions studied. The removal of the acid was always greater than the COD removal due to the formation of intermediate oxidation products, which are more refractory to oxidation than the initial product. Propionic acid, acetic acid, and acetone were found to be the main intermediates. The main finding of this work claims that two different activation energies are needed to represent the temperature dependence in two ranges, namely 200−275 °C and 275−320 °C. This finding can be explained by the competition between two main reaction pathways in the oxidation of the acid, although it has been stated that both pathways take place simultaneously at all temperatures. On the other hand, an unknown change in the species that govern the radical mechanism would also explain the results obtained, but further research is needed in order to understand better the complex chemistry of the process.

Acknowledgment

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