Contents lists available at ScienceDirect

Molecular Catalysis

journal homepage: www.journals.elsevier.com/molecular-catalysis

Transformation of biomass derivatives in aqueous medium: Oxidation of ethanol from sugarcane and acetol from biodiesel glycerol catalyzed by Fe^{3+} - H_2O_2

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ARTICLE INFO

Keywords: Ethanol oxidation Acetol oxidation Homogeneous catalysis Hydrogen peroxide

ABSTRACT

Ethanol obtained from sugarcane is an interesting biomass feedstock that is widely used as fuel and fuel additive. Another relevant biomass feedstock is acetol obtained from glycerol, the major byproduct of biodiesel manufacturing. Ethanol and acetol were oxidized by the $Fe(ClO_4)_3$ -H ClO_4 -H $_2O_2$ system in water at 60 °C with full conversions. Ethanol (0.1 M) oxidation yielded 0.058 M formic acid (HFO) and 0.085 M acetic acid (HAC), whereas acetol (0.1 M) oxidation provided 0.059 M HFO and 0.1 M HAC. On the basis of kinetic studies, the oxidation of these feedstocks followed different mechanisms. Ethanol oxidation followed a chain mechanism induced by hydroxyl radicals generated during the catalytic decomposition of H_2O_2 by Fe^{3+} . Acetol oxidation, on the other hand, followed a non-chain process in which the complex formed between acetol (as substrate) and the catalyst played a decisive role, and interaction between this complex and H_2O_2 was the limiting stage. The activation energies for ethanol and acetol oxidation were 24.1 and 14.8 kcal/mol, respectively.

1. Introduction

Today, humankind faces the challenges of reducing CO_2 emissions and decreasing dependence on fossil fuels [1]. The main strategy to mitigate these problems is to use biomass as feedstock to produce fuels and chemicals that can substitute the fuels and chemicals obtained from mineral sources, especially petroleum. Ethanol and biodiesel are two important products that can be obtained from biomass feedstock.

The current global production of ethanol is approximately 110 billion liters [2]. The United States are the major producer (54 %), with Brazil coming second (30 %). Despite having lost its position as the leading producer of ethanol, Brazil still presents the advantage of producing this fuel more competitively and without the need for direct government subsidies [3]. In addition, first-generation Brazilian sugarcane ethanol presents higher energy balance (amount of energy produced from sugarcane ethanol/amount of consumed fossil fuel

energy = 8.4) [4]. Ethanol is mainly applied as fuel (hydrated) and fuel additive (anhydrous). Ethanol can also be used to obtain building blocks such as ethylene, propylene, and 1,3-butadiene, which are currently obtained from petroleum, as well as oxygenated products, like acetal-dehyde, 1-butanol, ethyl acetate, and acetic acid [5–7]. Because ethanol is widely used as solvent and fuel, it could become a dangerous volatile organic compound (VOC). The most efficient way to remove VOCs is to conduct their catalytic oxidation to CO_2 , which has been a topic of several studies (for some examples, see [8–11]).

Biodiesel is another important product that can be obtained from biomass feedstock. Its global production was 41.3 billion liters in 2018 [12]. Increasing demand for biodiesel has generated a surplus of its major byproduct, glycerol, which has prompted numerous studies aiming at adding value to glycerol [13–17]. One possible route is to dehydrate glycerol to obtain acetol [18], which can then be used to obtain other products of industrial interest [19,20]. Acetol oxidation has

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https://doi.org/10.1016/j.mcat.2020.111307

Received 8 August 2020; Received in revised form 12 October 2020; Accepted 3 November 2020 Available online 21 December 2020 2468-8231/© 2020 Elsevier B.V. All rights reserved.





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been scarcely investigated. Some recent studies include the production of lactic acid over a Sn-Beta supported gold catalyst [21] and the oxidation of acetol as intermediate during the conversion of glycerol to formic acid and acetic acid by Lewis acid sites on ZrP- supported vanadium [22] and metal-free silica [23] catalysts.

One obstacle to the development of catalytic routes for chemical reactions is that many metallic catalysts are based on noble metals [24]; for example, palladium, rhodium, ruthenium, and iridium, which are expensive. To avoid the use of noble, rare, and expensive metals, various strategies for heterogeneous and homogeneous catalysis have been developed by using metals belonging to the first transition series. Among these metals, iron is particularly relevant because it is one of the most abundant metals on the Earth's crust, not to mention that it is inexpensive, relatively non-toxic, and versatile, as shown by the wide range of biological and man-made reactions mediated by iron [25–38].

Recently, we have reported that acetol oxidation by $FeCl_3-H_2O_2$ in acetonitrile, under mild conditions, yields formic and acetic acids as the main products [20]. By using 2-butanol as model, we have also reported that the same catalytic system works well for the oxidation of short-chain secondary alcohols in water [39].

Oxidation reactions that use the decomposition of H_2O_2 with a metallic catalyst are well known [40–45], and the use of H_2O_2 as a green oxidant (to generate H_2O as byproduct) has been extensively studied for the oxidation of alkanes [34,46–50], alkenes [51–55], and alcohols [37, 44,56–58]. Additionally, water is the most attractive solvent for green oxidations [59–63]. Therefore, the use of H_2O_2 as oxidant combined with low-cost and non-toxic iron as catalyst and water as solvent generates a greener oxidation system for alcohol oxidation. Moreover, the oxidation of organic compounds catalyzed by metal complexes can be significantly improved in the presence of additives, such as organic and inorganic acids and compounds containing nitrogen heterocycles [33, 34,48,56,64–66].

Here, we report the oxidation of renewable ethanol and acetol (a potential biodiesel waste) by $Fe(ClO_4)_3$ -HClO₄-H₂O₂ in aqueous medium, under mild conditions, and we examine the kinetics and mechanism of these reactions, which are still poorly explored in the literature and, in the case of acetol, have not been explored at all.

2. Material and experimental methods

2.1. Reactions and analyses

The reactions were conducted in a jacketed reactor at 60 °C, under air, in water. The following concentrations were used: 0.1 M ethanol or acetol, 0.5 M of H₂O₂, 0.03 M HClO₄, and 0.001 M Fe(ClO₄)₃. The volume of the reaction solution was 5 mL. For the gas chromatography (GC) analyses, the samples were prepared by adding 800 μ L of acetonitrile, 100 μ L of reaction solution, 100 μ L of a solution of nitromethane (internal standard), and a small amount of triphenylphosphine (to decompose H₂O₂ and stop the reaction) to a GC vial. The GC analyses were carried out using a Shimadzu GCMS-QP2010 chromatograph equipped with a SOLGEL-WAX column (30 m x0.25 mm x0.25 μ m) and a simple quadrupole MS detector.

The reactions that were performed to determine the initial rates involved changing the initial concentration of one of the reaction components or the temperature, while the other parameters were kept constant. The parameters range for the reactions that involved ethanol as substrate were: $[Fe(ClO_4)_3]_0$ within 0.3–5.0 M, $[Ethanol]_0$ within 0.05 – 0.5 M, $[H_2O_2]_0$ within 0.1–2.0 M and T within 50–70 °C. When acetol was the substrate, the parameters range were: $[Fe(ClO_4)_3]_0$ within 0.3–1.5 M, $[Acetol]_0$ within 0.1–0.6 M, $[H_2O_2]_0$ within 0.1–1.5 M and T within 50–80 °C. The samples were collected within the first 10 min of reaction and analyzed using a Shimadzu GC-2010 chromatograph equipped with an SGE BP-20 column (30 m x0.25 mm x0.25 µm) and an FID detector.

2.2. Determination of H_2O_2 concentration

The H₂O₂ concentration was determined by iodometric titration. The standard solution consisted of a 0.01 M Na₂S₂O₃ solution standardized with I₂ as primary standard. The sample was prepared by adding 1 mL of ethanol, 100 μ L of reaction solution, 1 mL of a 0.5 M H₂SO₄ solution, 0.12 g of KI, and three drops of a 3% m/v (NH₄)₆Mo₇O₂₄ catalyst solution into a 25-mL Erlenmeyer flask. The flask was then closed and left in the dark for 10 min to allow I₂ to form. The sample was then titrated with the Na₂S₂O₃ solution.

3. Results and discussion

3.1. Ethanol oxidation by Fe(ClO₄)₃-HClO₄-H₂O₂ system

Ethanol was oxidized by the Fe(ClO₄)₃-HClO₄-H₂O₂ system (Fig. 1). The main products were formic acid (HFO) and acetic acid (HAC). At the beginning of the reaction, acetaldehyde also emerged at low concentrations, but it was rapidly consumed. Under the studied conditions, the reaction system oxidized the substrate to full conversion within 30 min. The maximum HFO accumulation was 0.058 M at 30 min of reaction, which was equivalent to a turnover number (TON) of 58, whereas the maximum HAC accumulation was 0.085 M at 1 h of reaction (TON = 85). After these reaction times, strong over-oxidation occurred until 2 h of reaction, when almost all the H₂O₂ had been consumed (Fig. 2). After 2 h, the concentration of products, which slowly decompose, inducing the oxidation of HFO and HAC.

We calculated the turnover frequency (TOF) of this reaction for the time interval in which the conversion was close to 50 % (in this case, 2 min of reaction). The TOF was 656 and $372 \,h^{-1}$ for HFO and HAC, respectively.

3.2. Kinetics and mechanism of ethanol oxidation reaction

To understand the reaction mechanism better, we measured the initial reaction rate (W_0) when the initial concentration of the catalyst, substrate, and oxidant agent and the temperature were varied (Fig. 3) (more details can be found at the Supplementary Material). From the Arrhenius plot, we calculated the activation energy as 24.1 kcal/mol.

On the basis of the data in Fig. 1, ethanol disappeared before the



Fig. 1. Concentration of ethanol (curve 1), acetic acid (curve2), and formic acid (curve 3) during ethanol oxidation by $Fe(ClO_4)_3$ -HClO₄-H₂O₂. Conditions: 0.1 M ethanol, 0.001 M $Fe(ClO_4)_3$, 0.03 M HClO₄, and 0.5 M H₂O₂; T =60 °C.



Fig. 2. Concentration of $\rm H_2O_2$ during ethanol oxidation by $\rm Fe(\rm ClO_4)_3\text{-}HClO_4\text{-}H_2O_2\text{-}$ Conditions: 0.1 M ethanol, 0.001 M $\rm Fe(\rm ClO_4)_3$, 0.03 M $\rm HClO_4$, and 0.5 M $\rm H_2O_2\text{; }T$ =60 °C.

main reaction products were formed. In addition, at the initial stage in the process, acetaldehyde arose in the reaction medium (see Fig. 4), but it disappeared completely as the reaction proceeded.

These facts indicated that the organic acids originated from ethanol overoxidation; i.e., they were formed during oxidation of the primary alcohol conversion product, acetaldehyde. We observed a similar pattern during acetol oxidation. All the given kinetic regularities were obtained for the initial rates of decrease in substrate concentrations (W_0 = (-d[ROH]/dt)₀), when the concentrations of their overoxidation products were insignificant.

The mechanism of catalytic decomposition of H_2O_2 in acidified aqueous HClO_4 solutions in the presence of Fe(ClO_4)_3 was established in [67–69]. The process involves an ion radical chain, where the chain carriers are the radicals HO' and HO'_2 (the radical ion O_2^- , which is the product of acid HO'_2 dissociation) and the Fe^{2+} ion; their nucleation (initiation) is associated with transformations of the peroxo complex FeHO_2^{2+}. Formation of HO' radicals during the process is usually related to the oxidation of various organic compounds by systems containing iron ions and H_2O_2 [26,70,71]. Alcohols, and ethanol in particular, effectively interact with HO' radicals, to form r_α alcohol radicals (RO') [72]. In this regard, the kinetic models of HO' radicals induced by decomposition of H_2O_2 by Fe^{3+} ions and ethanol and acetol oxidation were considered and analyzed.

Before we consider the mechanism of the process, let us pay attention to the following facts. First, some of us have shown that addition of 0.02 M ethanol does not affect the rate at which tetranitromethane added to the Fe³⁺–H₂O₂–HClO₄ system is reduced at 25 °C [73]. According to [69], the tetranitromethane reduction rate corresponds to the initiation rate. Therefore, at 25 °C, ethanol does not affect the radical nucleation rate in the Fe^{3+} –H₂O₂–HClO₄ system. We assumed that, even at 60 °C, ethanol additives do not affect the radical nucleation rate. Then, using the results of [69], we calculated the radical nucleation rate for the experimental conditions in Fig. 3 and obtained an initiation rate value of 1.5×10^{-5} M s⁻¹ at 0.001 M Fe³⁺, 0.5 M H₂O₂, 0.03 M HClO₄, and 60 °C. Second, the initial ethanol consumption rate was 1.8×10^{-4} M s⁻¹ in these conditions. Hence, the chain mechanism of alcohol oxidation took place, which was reflected in the kinetic scheme presented below for the initial stages of the process. The scheme depicts the nucleation reactions (1,2) and the chain extension cycle for the catalytic decomposition of H_2O_2 by Fe^{3+} ions (3,4,5), the stage where alcohol oxidation is induced (6), the stage of chain alcohol oxidation (7,8,9), and the open circuit stage (10).

$$Fe^{3+} + H_2O_2 \rightleftharpoons FeHO_2^{2+} + H^+ K_1$$
 (1)

$$\operatorname{FeHO}_2^{2+} \to \operatorname{Fe}^{2+} + \operatorname{HO}_2^{\cdot} k_2 \tag{2}$$



Fig. 3. Plot of W₀ versus the initial concentration of the reaction components and of lnW_0 versus 1/T for the ethanol oxidation reaction. Conditions, except for the components being varied: 0.1 M ethanol, 0.001 M Fe(ClO₄)₃, 0.03 M HClO₄, and 0.5 M H₂O₂; T =60 °C.



Fig. 4. Acetaldehyde accumulation during ethanol oxidation by Fe(ClO₄)₃-HClO₄-H₂O₂ Conditions: 0.1 M ethanol, 0.001 M Fe(ClO₄)₃, 0.03 M HClO₄, and 0.5 M H₂O₂; T =60 °C.

$$Fe^{3+} + HO_2 \rightarrow Fe^{2+} + H^+ + O_2 k_3$$
 (3)

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + HO' k_4$$
 (4)

 $\mathrm{HO}' + \mathrm{H}_2\mathrm{O}_2 \to \mathrm{H}_2\mathrm{O} + \mathrm{HO}_2' \, k_5 \tag{5}$

 $\text{HO'} + \text{ROH} \rightarrow \text{H}_2\text{O} + r_{\alpha} k_6$ (6)

$$\mathbf{r}_{\alpha} + \mathbf{O}_2 \to \mathbf{r}\mathbf{O}_2 \ k_7 \tag{7}$$

 $rO_2 + ROH \rightarrow rOOH + r_{\alpha} k_8$ (8)

$$rO_2 \rightarrow CH_3 CHO + HO_2 k_9 \tag{9}$$

$$rO_2^{\bullet} + HO_2^{\bullet} \rightarrow \operatorname{Rooh} + O_2 k_{10}$$
(10)

Analysis of this kinetic scheme under the assumption that the concentration of chain carriers is quasi-stationary and that the oxidation chains are quite long, and given that the rate of reaction (5) is much lower than the rate of reaction (6), because k5 << k6 [72], leads to the following expression for the alcohol oxidation rate:

$$(-d[\text{ROH}]/dt)_0 = \{K_1k_2k_3k_9/(k_{10}[\text{H}^+])\}^{0.5} \times (k_8[\text{ROH}]/k_9 + 1) \times [\text{Fe}^{3+}] \times [\text{H}_2\text{O}_2]^{0.5}.$$
(11)

The expression obtained for the initial oxidation rate corresponded to the experimental data that were obtained for ethanol. Indeed, we verified a directly proportional dependence of the reaction rate on Fe³⁺ concentration, a linear dependence on alcohol concentration (see Figs. 3 and 4), and a root dependence on H_2O_2 concentration (see straight line 1 in Fig. 5).

In accordance with Eq. (11) and judging from the dependence shown in Fig. 5, the ratio between the rate constants k_8/k_9 was 11.8 M^{-1} at 60 °C. Moreover, on the basis of the value of the segment cutoff for this dependence on the ordinate axis, $\{K_1k_2k_3k_9 / (k_{10}) [\text{H}^+]\}^{0.5} \times [\text{Fe}^{3+}] \times [\text{H}_2\text{O}_2]^{0.5}$ was equal to $0.8 \times 10^{-4} \text{ M s}^{-1}$. By substituting the values of the concentrations of Fe^{3+} , H_2O_2 , and acid for the analyzed experiment, as well as the values of K_1 , k_2 , and k_3 calculated according to [69] for a temperature of 60 °C, we obtained a k_9/k_{10} value of $1.6 \times 10^{-6} \text{ M}$ for ethanol. Knowing that the effective activation energy of the ethanol oxidation process is 24.1 kcal/mol, we were able to roughly estimate the activation energy for the k_9/k_{10} ratio by assuming that the term in parentheses in expression (11) with [ROH] = 0.1 M weakly depended on temperature. By using the values for the equilibrium enthalpy (1) and activation energy of reactions (2 and 3) from [69], we obtained E_9 - E_{10} approximately equal to 13 kcal/mol.



Fig. 5. Dependence of $\log W_0$ on $\log [H_2O_2]$ for the ethanol (1) and acetol (2) oxidation reactions according to Figs. 3 and 8, respectively.

3.3. Acetol oxidation by Fe(ClO₄)₃-HC-HClO₄-H₂O₂ system

Acetol was oxidized by the Fe(ClO₄)₃-HClO₄-H₂O₂ system. The main products were HFO and HAC (Fig. 6). Full conversion was attained at 2 h of reaction, while the maximum HFO accumulation of 0.059 M was observed at 30 min of reaction (TON = 59), and the maximum HAC accumulation of 0.1 M was obtained at 2 h (TON = 100). After the maximum accumulation was reached, the concentration of products decreased as a consequence of their over-oxidation. H₂O₂ was almost entirely consumed within 4 h of reaction (Fig. 7). For longer reaction times (after 2 h), the concentration of products slightly decreases due to the formation of peroxide oxidation products, which slowly decompose, inducing the oxidation of HAC and HFO.

We calculated the TOF of this reaction for the reaction interval of 5 min, which was the interval when conversion was closer to 50 %. For HFO and HAC, the TOF was 276 and 363 h^{-1} , respectively.

3.4. Kinetics and mechanism of acetol oxidation reaction

As in the case of ethanol, we studied W_0 while the initial concentrations of acetol, H_2O_2 , and $Fe(ClO_4)_3$ and the temperature were varied



Fig. 6. Concentration of acetol (curve 1), formic acid (curve 2), and acetic acid (curve 3) during acetol oxidation by Fe(ClO₄)₃-HClO₄-H₂O₂. Conditions: 0.1 M acetol, 0.001 M Fe(ClO₄)₃, 0.03 M HClO₄, and 0.5 M H₂O₂; T = $60 \degree$ C.



Fig. 7. Concentration of $\rm H_2O_2$ during acetol oxidation $\rm Fe(ClO_4)_3-HClO_4-H_2O_2.$ Conditions: 0.1 M acetol, 0.001 M $\rm Fe(ClO_4)_3,$ 0.03 M HClO_4, and 0.5 M $\rm H_2O_2;$ T =60 $^\circ C.$

(Fig. 8) (more details can be found at the Supplementary Material). From the Arrhenius plot, we obtained an activation energy of 14.8 kcal/mol

A similar interpretation of the data for acetol discussed above met a number of objections. First, the effective order of the acetol oxidation rate as a function of the H₂O₂ concentration differed significantly from 0.5 (see straight line 2 in Fig. 5). Second, the effective activation energy of the reaction, 14.8 kcal/mol, was substantially lower than the activation energy of the ethanol oxidation reaction, 24.1 kcal / mol, and less than half the activation energy of the initiation process (Δ H1 + E2 = 32 kcal / mol), including stages (1,2).

Additionally, attention should be paid to the difference between ethanol and acetol as potential ligands capable of forming complexes with an iron ion. Unlike ethanol, acetol can coordinate with an iron ion via both its oxygen atoms. Compared to ethanol, the chelation effect will certainly increase the equilibrium constant for the formation of a complex between acetol and an iron ion significantly. These facts indicate that the mechanism of acetol oxidation should differ from the mechanism of ethanol oxidation.

The Fig. 8 illustrates the kinetic scheme that satisfactorily describes the observed kinetic laws if we assume that, at 60 °C and in the presence of acetol (R₁OH) and the Fe³⁺–H₂O₂–HClO₄ system, the role of the complex formed between the substrate and the iron ion becomes significant.

$$Fe^{3+} + R_1OH \Rightarrow Fe^{3+} \bullet R_1OH, \quad K_{12} = k_{+12}/k_{-12}$$
 (12)

Three routes of interaction of this complex with H_2O_2 can be suggested. The first involves formation of radicals HO[•] and $r_{1\alpha}$. The second involves formation of $r_{1\alpha}$ and Fe²⁺, which is rapidly oxidized by H_2O_2 , to generate HO[•] (reaction 4). The third involves formation of $r_{1\alpha}$ and ferryl ion FeO²⁺:

$$Fe^{3+} R_1OH + H_2O_2 \rightarrow Fe^{3+} + H_2O + HO' + r_{1\alpha}, k_{13}$$
 (13)

$$\rightarrow Fe^{2+} + H_2O_2 + H^+ + r_{1\alpha}$$
(14)

$$\rightarrow \text{FeO}^{2+} + \text{H}^+ + \text{H}_2\text{O} + r_{1\alpha}$$
(15)

The ferryl ion formed in (15) is then reduced by H_2O_2 in one of the possible ways:

$$\text{FeO}^{2+} + \text{H}_2\text{O}_2 + \text{H}^+ \to \text{Fe}^{3+} + \text{H}_2\text{O} + \text{HO}_2.$$
 (16)

$$FeO^{2+} + H_2O_2 \rightarrow Fe^{2+} + H_2O + O_2$$
 (17)



Fig. 8. Plot of W₀ versus the initial concentration of the reaction components and lnW_0 versus 1/T for the acetol oxidation reaction. Conditions, except for the components being varied: 0.1 M acetol, 0.001 M Fe(ClO₄)₃, 0.03 M HClO₄, and 0.5 M H₂O₂; T =60 °C.

 Fe^{2+} and HO₂ arising in stages (14, 16, 17) are subsequently converted into HO' by reactions (3) and (4), which induce R₁OH oxidation. These reactions are fast, so assuming that the concentration of the complex formed between the iron ion and alcohol is low and quasi-stationary, the rate at which the active species are generated by mechanism (12, 13), *W*i, can be represented as:

$$W_i = k_{+12} [\text{Fe}^{3+}] [\text{ROH}] / (1 + k_{-12} / k_{13} [\text{H}_2\text{O}_2])$$
(18)

If we assume that the rate of such path generating active particles substantially exceeds the rate of the traditional mechanism (reactions 1,2), the contribution of the chain transformation of the substrate to the observed oxidation rate should decrease. In other words, it can be accepted that a non-chain process of acetol oxidation takes place. In this case, the initial acetol oxidation rate is equal to twice the rate of generation of active particles (2*W*i). Accordingly, the observed acetol oxidation rate is directly proportional to the Fe³⁺ concentration (see Fig. 8). The experimental dependences on the R₁OH concentration were also close to the directly proportional dependence (see Fig. 8). The dependence of the oxidation rate on H₂O₂ concentration is well described by Eq. (18), which can be rearranged, to obtain linear Eq. (19):

From these data, the slope k_{+12} and the intercept $k_{\cdot 12}/k_{13}$ were1.4 M⁻¹ s⁻¹ and 0.19 M, respectively (Fig. 9).

Fig. 10 presents the value that was calculated from Eq. (18), plotted alongside the experimental values. The good correlation further validated the equation and the constants.

3.5. Comparison between the ethanol and acetol oxidation mechanisms

We propose two different mechanisms for the oxidation of ethanol and acetol. In the initial stages of both oxidation mechanisms (see Sections 3.2 and 3.4.), both ethanol and acetol are activated by formation of the corresponding alpha-alcohol radicals (CH3C'HOH and CH3COC'HOH). In the first case, the dominant route for their formation is interaction with radicals HO' (reaction 6) arising during the catalytic decomposition of H_2O_2 by iron ions. In the second case, the interaction of the Fe³⁺-acetol complex with H_2O_2 (reaction15, Scheme 1) prevails.

The resulting alpha-alcohol radicals interact with O₂, to form the corresponding peroxide radicals. In the case of ethanol, its peroxide radicals participate mainly in the chain extension reaction, with formation of hydroperoxide (reaction 8), or they decompose during the



Fig. 9. Plot of $[H_2O_2]/W_0$ versus $[H_2O_2]$ for the acetol oxidation reaction. Conditions: 0.1 M acetol, 0.001 M Fe(ClO₄)₃, 0.03 M HClO₄, and 0.1 to 1.5 M H_2O_2 ; T =60 °C.



Fig. 10. Plot with values calculated from Eq. (18) and experimentally obtained values. Conditions: 0.1 M acetol, 0.001 M Fe(ClO₄)₃, 0.03 M HClO₄, and 0.1 to 2.0 M H_2O_2 ; T =60 °C.

monomolecular reaction, to form acetaldehyde and HO₂ (reaction 9), which participates in the chain extension cycle (reactions 3,4,6). The acetol peroxide radicals are mainly reduced to peroxide ($r_{1\alpha}O_2 + e^- + H^+ \rightarrow r_{1\alpha}O2H$). Further transformations of the resulting peroxides and acetaldehyde oxidation induced by HO[•] produce the reaction products – formic and acetic acids. Further oxidation of these products, induced by HO[•], occurs under excess H₂O₂.

4. Conclusions

We have found that a simple and low-cost catalytic system Fe $(ClO_4)_3$ -HClO₄-H₂O₂ effectively oxidizes ethanol in aqueous solution under mild conditions. Acetic and formic acids are the main products from both substrates. In the two reactions, acetaldehyde is an intermediate compound. The reaction rates depend on the initial concentrations of each reagent. On the basis of a kinetic study of these data, the ethanol and acetol oxidation reactions follow different mechanisms. In the case of ethanol, oxidation occurs via a radical chain mechanism. Acetol is oxidized via interaction of the Fe³⁺-acetol chelate complex with H₂O₂. This catalytic system may have good perspectives in industrial waste processing for the production of diesel fuel and sugars.

CRediT authorship contribution statement

Marcos Lopes de Araújo: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Writing - original draft, Writing review & editing. Gilvan Aguiar Correia: Methodology, Writing - review & editing. Wagner Alves Carvalho: Resources, Funding acquisition. Lidia Sergeevna Shul'pina: Conceptualization, Writing - review & editing. Yuriy Nikitovich Kozlov: Formal analysis, Funding acquisition, Writing - original draft, Writing - review & editing. Georgiy Borisovich Shul'pin: Conceptualization, Methodology, Funding acquisition, Supervision, Writing - original draft, Writing - review & editing. Dalmo Mandelli: Conceptualization, Resources, Methodology, Funding acquisition, Supervision, Writing - original draft, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial



Scheme 1. Proposed mechanism of the acetol oxidation.

interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

D. M. and W. A. C. thank projects CNPq 309570/2016-6, CNPq 422290/2016-5, CNPq 404843/2018-2, FAPESP 2018/01258-5, 2017/ 24931-4, and the Sustainable Technologies Unit of UFABC (NuTS). This study was partially funded by Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) - Finance Code 001. The publication was prepared with the financial support of RFBR according to Research Project 19-03-00142. This work was performed within the framework of the Program of Fundamental Research of the Russian Academy of Sciences for 2013-2020 on the research issue of IChP RAS No. 47.16. Theme number in Federal Agency for Scientific Organizations: 0082-2014-0004. State registration number of Center of Information Technologies and Systems for Executive Power Authorities (CITIS): AAAA-A17-117040610283-3. L.S.S. thanks INEOS RAS for supporting part of the study.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mcat.2020.111307.

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