

Catalytic Conversion of Dihydroxyacetone to Lactic Acid with Brønsted Acids and Multivalent Metal Ions

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The exploitation of by-products from chemical processes shows high potential for the development of new synthesis routes for valuable chemicals. Glycerol, provided as a by-product from the biodiesel manufacturing process, is a potential feedstock chemical. From dihydroxyacetone, a primary oxidation product of glycerol, lactic acid may be obtained. The catalytic effect of Brønsted acids and multivalent metal ions on the conversion of dihydroxyacetone to lactic acid in aqueous solutions was investigated. Lactic acid yields of 83 % were achieved when carrying out the reaction under reflux boiling conditions with the catalyst HCl in excess. High acidity of the reaction solution is essential for the dehydration of dihydroxyacetone to pyruvic aldehyde. Consecutive conversion of pyruvic aldehyde to lactic acid was accelerated by multivalent metal ions (e.g. Al^{3+}). The Lewis acid $Al_2(SO_4)_3$ provides both acidic reaction conditions for dehydration of dihydroxyacetone to pyruvic aldehyde and acceleration of lactic acid formation from pyruvic aldehyde. Lactic acid yields of up to 78 % were obtained with $Al_2(SO_4)_3$.

Key words:

lactic acid, Brønsted acid, Lewis acid, dihydroxyacetone, glycerol

Introduction

At present, a vast majority of products such as plastics, cosmetics or pharmaceuticals are still petroleum-based. A shift towards renewable bio-based feedstock will be inevitable in the future. However, the use of biomass for chemical production implicates the redesign of existing processes and involves new challenges. Handling of aqueous reaction systems and the need for adapted separation techniques from aqueous solutions come to the fore. Retrieval of biomass which does not compete with the food production draws attention to the exploitation of residual materials. Glycerol (propane-1,2,3-triol) is a versatile molecule obtained as a by-product in the biodiesel manufacturing process. Due to increasing biodiesel production over the last decades, it may be regarded as a potential renewable feedstock chemical. Exploitation of glycerol for the production of lactic acid is a promising approach.

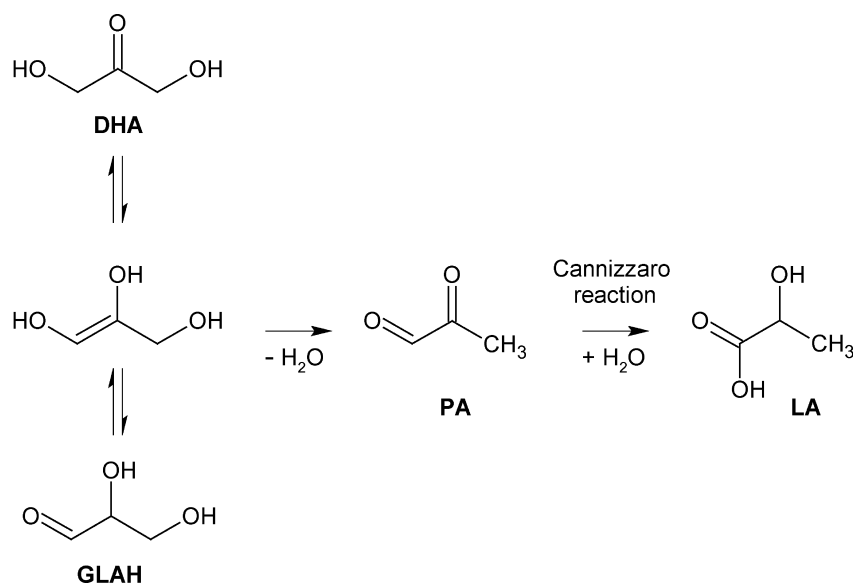
Lactic acid (2-hydroxypropionic acid) is emerging as a building block in a new generation of bio-based materials. With both a hydroxyl and a carboxylic acid group, lactic acid may undergo many reactions. It therefore represents a central feedstock for the chemical industry, e.g., in the production of propylene glycol, acrylic acid or different condensation products. Besides applications in the food

and cosmetics industries, growth in demand is expected due to expanding polymer markets (biodegradable synthetics) and elevated demand in the chemical sector due to ecologically friendly solvents and oxygenated chemicals.^{1,2} Nevertheless, commercial success depends on the development of an effective production method for highly pure lactic acid from abundant non-food biomass.

Oxidation of one of the three alcoholic functions of glycerol gives access to the synthesis of the trioses dihydroxyacetone (1,3-dihydroxypropan-2-one, DHA) and glyceraldehyde (2,3-dihydroxypropanal, GLAH), which may further be catalytically converted to lactic acid.

Dihydroxyacetone from glycerol is accessible via different synthesis routes. Chemical synthesis involves liquid phase self-condensation of formaldehyde with thiazolium catalysts.³ Much research has been done in the area of noble metal catalysed oxidation of glycerol.^{4–6} Partial electrochemical oxidation of glycerol to dihydroxyacetone is carried out with different electrode types in neutral⁷, alkaline^{8–11} and acidic media^{10,11}. The first microbiological dehydration of glycerol to dihydroxyacetone was reported in 1898 by Bertrand.¹² Since then, several routes for microbiological synthesis of dihydroxyacetone have been developed and patented. Mainly vinegar bacteria type *Acetobacter* and *Gluconobacter* are used.^{13,14}

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Scheme 1 – Conversion of dihydroxyacetone (DHA) and glyceraldehyde (GLAH) to lactic acid (LA)

Non-fermentative catalytic chemical conversion of dihydroxyacetone and glyceraldehyde to lactic acid or lactate is currently gaining great interest in both academia and industry. The reaction proceeds via dehydration of the triose yielding pyruvic aldehyde (2-oxopropanal, PA) as intermediate (Scheme 1). Subsequent conversion of pyruvic aldehyde to lactic acid is an intramolecular Cannizzaro type rearrangement reaction. The key reaction step is the shift of a hydride.¹⁵

Conversion properties of dihydroxyacetone to pyruvic aldehyde under acid exposure were first mentioned by Pinkus¹⁶ in 1898. Prey *et al.*¹⁵ reported the formation of lactic acid when treating dihydroxyacetone, glyceraldehyde and pyruvic aldehyde with acids. Acid catalysed isomerization of glyceraldehyde and dihydroxyacetone and dehydration to pyruvic aldehyde were investigated by Lookhart and Feather¹⁷. Strongly acidic operating conditions favour dehydration. The rate of dihydroxyacetone dehydration is higher than the rate of glyceraldehyde dehydration.

The use of heterogeneous Brønsted and Lewis acid catalysts and the use of homogeneous multivalent metal salts as catalysts have been reported in literature. Heterogeneous catalysts include zeolites¹⁸, hydroxyapatite-supported Lewis acids¹⁹, substituted mesoporous MCM-41 materials²⁰, and tin ion-exchanged montmorillonite²¹. Their application is limited to lactate synthesis in alcoholic medium as coking and irreversible structural modifications occur in aqueous solutions. These result in deactivation of the heterogeneous catalysts when the reaction is carried out in water for lactic acid synthesis.^{18,20} For the exploitation of biomass derived precursors, the handling of aqueous reaction systems is crucial.

Bicker *et al.*²² investigated the catalytic effect of the metal ions Co²⁺, Ni²⁺, Cu²⁺, and Zn²⁺ on the formation of lactic acid from hexoses and trioses in sub- and supercritical water. Zn²⁺ gave the best results with a lactic acid yield of 86 % (g g⁻¹) from dihydroxyacetone at 300 °C (*p* = 25 MPa). Rasrendra *et al.*²³ presented a study of the catalytic effect of 26 metal salts on the conversion of dihydroxyacetone and glyceraldehyde to lactic acid in water. A temperature range of 120–180 °C was investigated. Al³⁺ salts were identified as the most promising catalysts with lactic acid yields of >90 % at 140 °C and a reaction time of 90 minutes.

These studies highlight that both acids and multivalent metal ions are capable of catalysing lactic acid formation from dihydroxyacetone. However, an investigation of liquid phase synthesis of lactic acid from dihydroxyacetone at moderate temperatures (room temperature to reflux boiling conditions at ambient pressure) is still lacking. Apart from potential energy savings and equipment simplifications, by-product formation is generally reduced or even suppressed at lower reaction temperatures. For this reason, an extensive study on liquid phase conversion of dihydroxyacetone to lactic acid in aqueous solution was conducted. The Brønsted acids HCl, H₂SO₄, H₃PO₃, the strongly acidic ion exchange resin Lewatit®K2620, and acidic hydrolysing metal salts were used as catalysts. The investigation of the conversion behaviour of dihydroxyacetone in acidic aqueous medium is especially relevant, as biomass derived precursors are often obtained after acid treatment of biomass. Consequently, both water and acid are present in the reaction solution. Furthermore, concurrence of homogeneous Brønsted acids with multivalent metal ions was discussed. The reaction kinetics with different catalysts was modelled and the most promising catalyst was identified.

Experimental

Chemicals

Dihydroxyacetone (dimer, puriss.) was supplied by Merck. Pyruvic aldehyde (~40 % in H₂O) was provided by Sigma-Aldrich. Lactic acid in aqueous solution (1 mol L⁻¹) was provided by Riedel-de Haën. Hydrochloric acid (HCl, 37 %, p.a.) and sulphuric acid (H₂SO₄, 95 %) were purchased from Carl Roth. H₃PO₄ (85 %) was purchased from Merck. Metal salts Al₂(SO₄)₃·16H₂O (≥95 %, p.a.) and ZnSO₄·7H₂O (≥99.5 %, p.a.) were supplied by Carl Roth, SnCl₂·2H₂O (≥98 %, p.a.), Al(NO₃)₃·9H₂O (≥98.5 %, p.a.), CrCl₂ (90 %), and ZrOCl₂·8H₂O (≥99 %, pro analysi) by Merck, AlCl₃ (≥99.9 %) by Sigma Aldrich; Cr₄(SO₄)₅(OH)₂ (100 %) by Riedel-de Haën; and CuSO₄ (99 %, pur) by Fluka. The ion exchange resin Lewatit®K2620 (cation exchange capacity ≥ 5.2 eq kg⁻¹) was provided by Lanxess. All chemicals, except the ion exchange resin, were used without further pretreatment. The ion exchange resin was washed with deionized water until the supernatant liquid was colourless and the pH neutral. Then it was vacuum dried until its mass remained constant.

Aqueous solutions of dihydroxyacetone were prepared by dissolving dimeric dihydroxyacetone in deionized water. Dissolution results in the monomerisation of the dimeric form.²⁴ In most experiments, the concentration of dihydroxyacetone was 50 g L⁻¹ (0.56 mol L⁻¹). This value is representative for dihydroxyacetone solutions derived from the fermentation of glycerol.

Experimental setup

Homogeneous catalytic experiments were carried out in batch mode in reactors (500 mL) equipped with a reflux condenser, heating coil, and magnetic stirrer (Heidolph MR 3003 control). Homogeneous catalysts included mineral acids and soluble metal salts. The reaction was started by admixture of preheated catalyst and feed solutions. The reaction temperature was controlled and kept constant throughout the reaction (± 0.5 °C).

For loading of Lewatit®K2620 with Al³⁺, the sodium form of the macroporous resin was used. The loading procedure included stirring of Lewatit®K2620 in aqueous solutions of Al₂(SO₄)₃·16H₂O at room temperature for five hours, washing with deionised water and drying in a vacuum dryer until its mass remained constant. Excess of the metal ions Al³⁺ was assured. At least a threefold molar amount of Al³⁺ was provided per mole of functional resin site. This procedure was carried out twice.

Experiments with aluminium-laden Lewatit®K2620 were carried out in batch mode in reac-

tors (2 L) equipped with a reflux condenser, heating coil, and stirrer with a PTFE stirring blade. The reaction was started by admixture of the catalyst to the preheated feed. The reaction temperature was controlled and kept constant throughout the reaction (± 0.5 °C).

For reuse of the aluminium-laden resin, the resin was separated from the reaction mixture, washed with deionised water, vacuum dried and used again.

Experiments were replicated at least three to five times. Mean deviation of dihydroxyacetone, pyruvic aldehyde and lactic acid concentrations were below 3 %, respectively. Results are given as mean values.

Analytcs

Dihydroxyacetone, the intermediate pyruvic aldehyde and the product lactic acid were quantitatively analysed by high-performance liquid chromatography (Ultimate 3000, Dionex). The substances were separated with the columns Rezex ROA Organic Acid H⁺ (Phenomenex) and Acclaim OA (Dionex). Detection was carried out with a variable wavelength UV/VIS detector at 190 nm and 210 nm (Dionex). For elution of the substances from Rezex ROA 0.005 mol L⁻¹ H₂SO₄ at 50 °C was used. From Acclaim OA column substances were eluted with 0.1 mol L⁻¹ Na₂SO₄ (pH 2.65) at 30 °C. The pH was adjusted with methane sulphonic acid.

Modelling of the reaction kinetics

Lactic acid formation from dihydroxyacetone was formally best modelled as a dual step consecutive reaction. Both reaction steps are first order with respect to the corresponding educt. According to the mechanism shown in Equation 1, k_1 is the rate constant for the conversion of dihydroxyacetone to pyruvic aldehyde, k_2 the rate constant for the consecutive conversion of pyruvic aldehyde to lactic acid.



Kinetics of by-product formation was not modelled but taken into account through implementation of the selectivity factor S . S represents the molar fraction of feed dihydroxyacetone, which is converted to pyruvic aldehyde and lactic acid via dehydration and Cannizzaro rearrangement, respectively.

The conversion of acetic acid was modelled according to Equation 2.

$$c_{\text{DHA}} = c_{\text{DHA},0} \cdot e^{-k_1 t} \quad (2)$$

The rate constant k_1 was derived by minimizing the mean squared deviation of the calculated and

the measured dihydroxyacetone concentrations. The formation and conversion of pyruvic aldehyde was modelled according to Equation 3. After determination of k_1 , k_2 and S_{PA} were derived by the method of least squares with respect to calculated and experimental pyruvic aldehyde concentrations.

$$c_{PA} = \frac{c_{DHA,0} \cdot S_{PA} \cdot k_1}{k_2 - k_1} \cdot (e^{-k_1 t} - e^{-k_2 t}) \quad (3)$$

Lactic acid formation was modelled according to Equation 4.

$$c_{LA} = c_{DHA,0} \cdot S_{LA} \cdot \left[1 + \frac{1}{k_1 - k_2} \cdot (k_2 \cdot e^{-k_1 t} - k_1 \cdot e^{-k_2 t}) \right] \quad (4)$$

With known rate constants k_1 and k_2 , S_{LA} was derived by minimizing the mean squared deviation of the calculated and the measured concentrations of lactic acid.

Temperature dependence of k_1 and k_2 was based on Arrhenius' law (Equation 5).

$$k = A \cdot e^{-\frac{E_A}{R \cdot T}} \quad (5)$$

Results and discussion

Catalysis with Brønsted acids

The catalytic effect of the homogeneous Brønsted acids HCl, H_2SO_4 , and H_3PO_4 on the formation of lactic acid was investigated. The ion exchange resin Lewatit®K2620 was used as a heterogeneous Brønsted acid catalyst. Moreover, the autocatalytic effect of lactic acid was screened.

Comparison of different Brønsted acids

For comparison of the catalytic effect of the Brønsted acids HCl, H_2SO_4 , and H_3PO_4 on the formation of lactic acid, experiments were performed at reflux boiling conditions with dihydroxyacetone concentrations of 0.56 mol L^{-1} and acid concentrations of $c_{H^+} = 1 \text{ mol L}^{-1}$, respectively. For investigation of the autocatalytic effect of lactic acid, experiments were performed under the same reaction conditions ($c_{DHA,0} = 0.56 \text{ mol L}^{-1}$, reflux boiling conditions) and an initial lactic acid concentration of 1 mol L^{-1} .

High acidity of the reaction solution results in fast conversion of dihydroxyacetone. As depicted from Table 1, the rate of dihydroxyacetone conversion increases with increased acidity.

Table 1 – Catalytic effect of different Brønsted acids on the conversion of dihydroxyacetone (X_{DHA}) and the yields of pyruvic aldehyde (Y_{PA}) and lactic acid (Y_{LA}) after a reaction time of 1 h and 6 h ($c_{DHA,0} = 0.56 \text{ mol L}^{-1}$, $c_{H^+} = 1 \text{ mol L}^{-1}$, reflux boiling conditions)

Catalyst	X_{DHA} %	Y_{PA} %	Y_{LA} %	X_{DHA} %	Y_{PA} %	Y_{LA} %
	1 h			6 h		
Lactic acid ^[a]	9	7	2	39	26	4
HCl ^[a]	100	87	7	100	54	30
H_2SO_4 ^[a]	100	87	4	100	54	19
H_3PO_4 ^[a]	32	23	≤ 0.1	85	65	1
Lewatit®K2620 ^[b]	88	88	≤ 1	100	72	28

^[a]100 °C ^[b]98 °C

With HCl and H_2SO_4 as the strongest acids, dihydroxyacetone was completely converted within one hour. The yields of lactic acid were 7 % and 4 %, respectively. After a reaction time of six hours, lactic acid yields were 30 % with HCl and 19 % with H_2SO_4 . From the results in Table 1, it can be depicted that after six hours, 16 % of dihydroxyacetone must have reacted to unfavourable by-products when using HCl as catalyst. With H_2SO_4 , 27 % of dihydroxyacetone (on a molar basis) must have been converted to by-products after six hours.

In contrast to complete conversion within one hour with HCl and H_2SO_4 , only 32 % of dihydroxyacetone were converted with H_3PO_4 and 88 % with Lewatit®K2620. Lactic acid was not formed in remarkable amounts (≤ 1 %) during that time. With H_3PO_4 , the yield of lactic acid was still low (1 %) after six hours, whereas with Lewatit®K2620 yields of 28 % could be achieved. Limited lactic acid yields of 28 % are dedicated to the lower rates of reaction with Lewatit®K2620. According to the material balance, no by-product formation was observed during a reaction time of six hours. Furthermore, easy separation from the reaction mixture and reusability of Lewatit®K2620 are advantageous. No loss of catalytic activity was observed after repeated use under the conditions specified (six times for six hours).

The autocatalytic effect of lactic acid on the conversion of dihydroxyacetone was also investigated. After one hour, 9 % of dihydroxyacetone were converted when lactic acid was present in the feed solution. Due to its lower acidity, the yields of lactic acid were limited to 2 % after a reaction time of one hour.

This shows the high impact of acidity on the rates of conversion. High acidity of the reaction solution favours both conversion of dihydroxyacetone and consecutive rearrangement of pyruvic al-

dehyde to lactic acid. Highest lactic acid yields were achieved with HCl due to its high acidity. Since the highest reaction rates and higher selectivities towards lactic acid in contrast to the catalyst H_2SO_4 were achieved with HCl, further investigations were based on HCl as catalyst.

Catalysis with HCl

Figure 1 representatively shows the conversion of dihydroxyacetone to lactic acid via the intermediate pyruvic aldehyde with HCl. Dihydroxyacetone was completely converted within 10 minutes when carrying out the reaction with 3 mol L^{-1} HCl and boiling under reflux conditions. Subsequent conversion of the intermediate pyruvic aldehyde to lactic acid was rate determining. The rate of lactic acid formation was low at the beginning. This period of induction is characteristic for consecutive reactions. Isomeric glyceraldehyde was not detected in remarkable amounts.

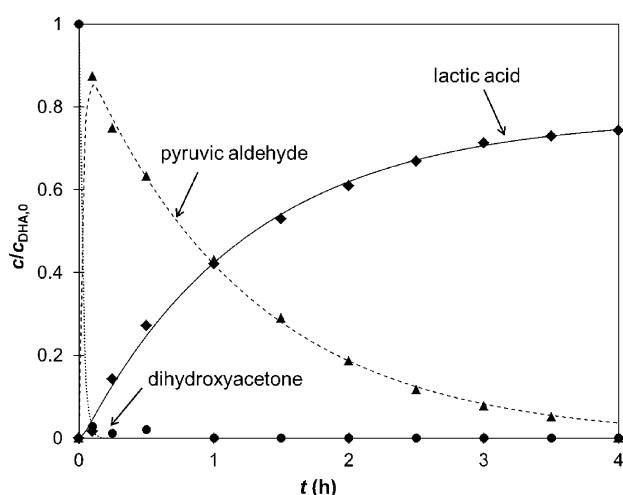


Fig. 1 – Conversion of dihydroxyacetone to lactic acid via the intermediate pyruvic aldehyde with HCl ($c_{\text{DHA},0} = 0.56 \text{ mol L}^{-1}$, $c_{\text{HCl}} = 3 \text{ mol L}^{-1}$, boiling at reflux conditions, ambient pressure)

With HCl, the transparent reaction solution changed colour to yellow and brownish with progress in reaction. Polymerized pyruvic aldehyde is assumed to be responsible for the change in colour. Dark brown to black precipitates segregated at high acid concentrations and high reaction temperatures. This was also observed for catalysis with H_2SO_4 and H_3PO_4 . Hahn and Schales²⁵ described precipitates similar to the species found in this project as segregated acids with humic acid-like properties.

Effect of reaction temperature

The liquid-phase conversion of dihydroxyacetone to lactic acid with HCl was investigated in a temperature range of $25 \text{ }^\circ\text{C}$ to $100 \text{ }^\circ\text{C}$. The yield of lactic acid at different reaction temperatures can be

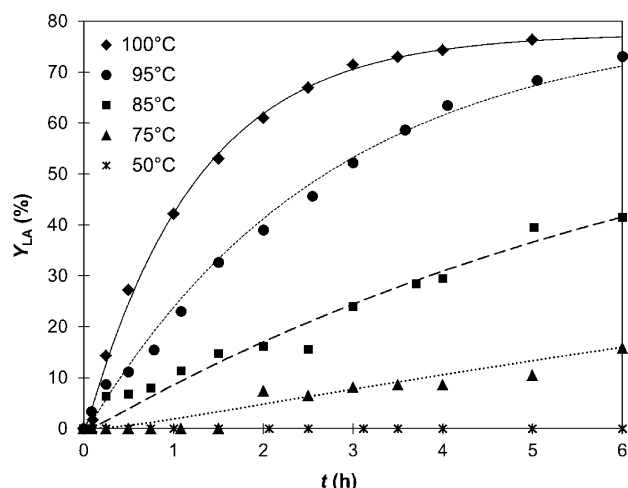


Fig. 2 – Effect of the reaction temperature on the yield of lactic acid (LA) with HCl ($c_{\text{DHA},0} = 0.56 \text{ mol L}^{-1}$, $c_{\text{HCl}} = 3 \text{ mol L}^{-1}$)

depicted from Figure 2. The effect of the reaction temperature on intermediate formation of pyruvic aldehyde and its consecutive conversion can be seen in Figure 3. The initial dihydroxyacetone concentration was 0.56 mol L^{-1} in those experiments; HCl concentration was 3 mol L^{-1} .

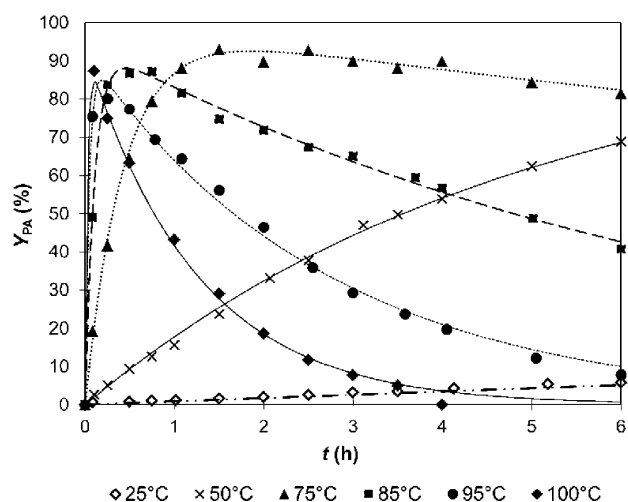


Fig. 3 – Effect of the reaction temperature on the yield of pyruvic aldehyde (PA) with HCl ($c_{\text{DHA},0} = 0.56 \text{ mol L}^{-1}$, $c_{\text{HCl}} = 3 \text{ mol L}^{-1}$)

The yield of lactic acid increased significantly with increasing reaction temperatures. No lactic acid formation was observed for six hours when carrying out the reaction below $50 \text{ }^\circ\text{C}$. As expected from the negligible lactic acid formation, formation of pyruvic aldehyde was suppressed at low temperatures ($25 \text{ }^\circ\text{C}$), too. The yield of pyruvic aldehyde was less than 6 % after six hours at $25 \text{ }^\circ\text{C}$. At $50 \text{ }^\circ\text{C}$, 70 % of dihydroxyacetone was converted after six hours. A yield of 70 % of pyruvic aldehyde after six hours showed that by-product formation

from dihydroxyacetone was negligible at these reaction conditions resulting in complete conversion of dihydroxyacetone to pyruvic aldehyde. However, lactic acid formation was suppressed due to the low reaction temperature.

At 75 °C, the yield of lactic acid was still low (16 %) after six hours. A remaining pyruvic aldehyde concentration of 0.46 mol L⁻¹ and complete conversion of dihydroxyacetone within 2.5 hours indicated that by-product formation was still of minor relevance (below 2 %).

Complete conversion of dihydroxyacetone was achieved within 45 minutes at 85 °C and within 10 minutes at 100 °C. At 100 °C, the peak pyruvic aldehyde concentration was obtained within 5 minutes. Consecutive rearrangement to lactic acid was completed within 6 hours. The yield of lactic acid was 78 %.

The temperature dependency was modelled according to Arrhenius' law (Figure 4). Table 2 lists the activation energies E_A and pre-exponential factors A for both reaction steps. Activation energies and the pre-exponential factors confirm that lactic acid formation from pyruvic aldehyde is rate-determining. From the Arrhenius' plot, no change of reaction mechanism within the investigated temperature range could be deduced.

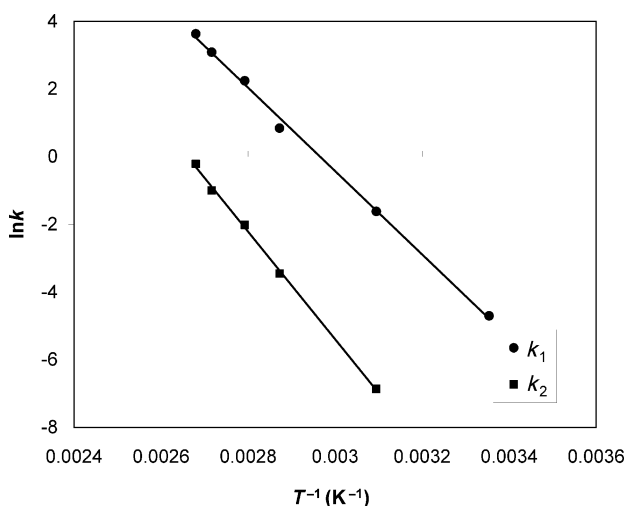


Fig. 4 – Arrhenius' plot for the first (dihydroxyacetone to pyruvic aldehyde) and second (pyruvic aldehyde to lactic acid) reaction step ($c_{\text{HCl}} = 3 \text{ mol L}^{-1}$, $c_{\text{DHA},0} = 0.56 \text{ mol L}^{-1}$)

Table 2 – Activation energies E_A and pre-exponential factors A for the HCl catalysed conversion of dihydroxyacetone to lactic acid ($c_{\text{HCl}} = 3 \text{ mol L}^{-1}$, $c_{\text{DHA},0} = 0.56 \text{ mol L}^{-1}$)

	$A \text{ (h}^{-1}\text{)}$	$E_A \text{ (kJ mol}^{-1}\text{)}$
1. DHA → PA	$(7.29 \pm 0.02) \cdot 10^{15}$	102.4 ± 0.3
2. PA → LA	$(2.35 \pm 0.01) \cdot 10^{18}$	132.2 ± 0.4

Effect of HCl and feed dihydroxyacetone concentrations

At a fixed feed dihydroxyacetone concentration of 0.56 mol L⁻¹ HCl concentrations were varied between 0.5 mol L⁻¹ and 5 mol L⁻¹, respectively. According to the HCl concentrations in the solution, a boiling point temperature between 98 °C and 104 °C was observed.

Figure 5 shows the strong impact of the acidity of the reaction solution on the rate of lactic acid formation again.

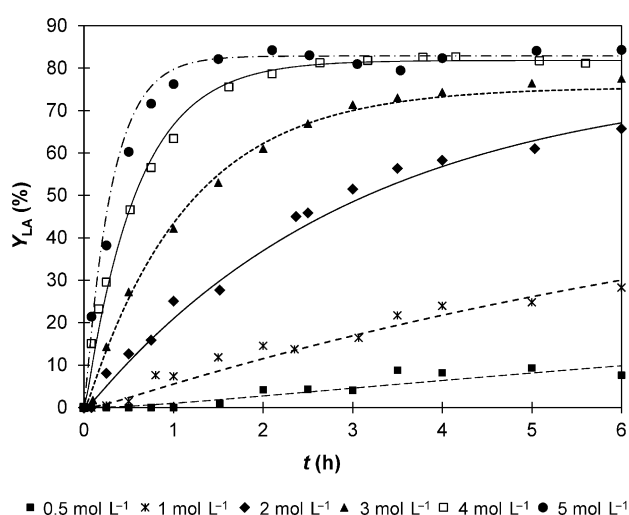


Fig. 5 – Effect of HCl concentrations on the yield of lactic acid at operation under reflux boiling conditions ($c_{\text{DHA},0} = 0.56 \text{ mol L}^{-1}$; 98 °C ($c_{\text{HCl}} = 0.5 \text{ mol L}^{-1}$), 99 °C ($c_{\text{HCl}} = 1 \text{ mol L}^{-1}$), 100 °C ($c_{\text{HCl}} = 2 \text{ mol L}^{-1}$), 101 °C ($c_{\text{HCl}} = 3 \text{ mol L}^{-1}$), 103 °C ($c_{\text{HCl}} = 4 \text{ mol L}^{-1}$) and 104 °C ($c_{\text{HCl}} = 5 \text{ mol L}^{-1}$))

HCl concentrations of 0.5 mol L⁻¹ resulted in complete conversion of dihydroxyacetone within three hours. The results indicated that dihydroxyacetone was entirely converted to pyruvic aldehyde. Increasing HCl concentrations to 1 mol L⁻¹ reduced the time for complete conversion of dihydroxyacetone to one hour. With HCl in a concentration of 5 mol L⁻¹ complete dihydroxyacetone conversion was achieved within 5 minutes.

Apart from higher reaction rates, increasing HCl concentrations resulted in increasing lactic acid selectivity. This indicates that by-product formation from pyruvic aldehyde is suppressed at high acid concentrations. With 5 mol L⁻¹ HCl, the final lactic acid yield was 83 %. Subsequent degradation of lactic acid was not observed.

The validity of the rate law for different dihydroxyacetone concentrations was investigated from 25 g L⁻¹ (0.28 mol L⁻¹) to 75 g L⁻¹ (0.83 mol L⁻¹) and a constant HCl concentration of 3 mol L⁻¹ at 101 °C. In a second series of experiments, the validity of the rate law was tested for varying feed dihydroxyacetone concentrations but constant 5.4-fold

molar excess of H^+ with respect to feed dihydroxyacetone at 101 °C.

Again, it was confirmed that the HCl concentration in the aqueous solution has a major impact on the rate of lactic acid formation. Acidity of the reaction mixture consequently has a high impact on lactic acid formation. Highest lactic acid formation rates were obtained at high HCl concentrations. With 75 g L⁻¹ dihydroxyacetone and 4.5 g L⁻¹ HCl in the feed, the yield of lactic acid was 50 % after 30 minutes and a final lactic acid yield of 78 % was achieved within three hours. After three hours, the yield of lactic acid was 71 % with 50 g L⁻¹ dihydroxyacetone and 3 mol L⁻¹ HCl in the feed, and 36 % with 25 g L⁻¹ dihydroxyacetone and 1.5 mol L⁻¹ HCl.

At constant HCl concentration and varying feed dihydroxyacetone concentrations, the yield of lactic acid decreases with increasing dihydroxyacetone concentration. By material balance, the portion of dihydroxyacetone which was converted to pyruvic aldehyde and lactic acid, respectively, was determined. With 25 g L⁻¹ feed dihydroxyacetone 87 % of dihydroxyacetone were converted to pyruvic aldehyde and lactic acid after a reaction time of six hours. In contrast to this, the percentage was lower with 50 g L⁻¹ (77 %) and 75 g L⁻¹ (75 %).

Concurrence of Brønsted acid catalysts and multivalent metal ions

Experiments with multivalent metal ions Zn²⁺, Sn²⁺, Fe²⁺, Fe³⁺, Al³⁺, Cr²⁺, and Cr³⁺ revealed different catalytic effects on the acid catalysed conversion of dihydroxyacetone to lactic acid. Experiments were performed with 0.56 mol L⁻¹ feed concentrations of dihydroxyacetone, acid concentrations of 1 mol H⁺ L⁻¹ plus catalytic amounts of metal ions at 99 °C. The conversion of dihydroxyacetone and yields of pyruvic aldehyde and lactic acid are compared in Table 3 for the various metal salts after a reaction time of one hour.

For combinations of Brønsted acids and metal ions, the highest catalytic effect on lactic acid formation was observed with Sn²⁺. With HCl/Sn²⁺ both dihydroxyacetone and pyruvic aldehyde were completely converted within one hour. A final lactic acid yield of 75 % was achieved after one hour. In contrast, the yield of lactic acid after one hour was 7 % for HCl catalysis without Sn²⁺. It was shown that the addition of catalytic amounts of Sn²⁺ to the HCl catalysed reaction had a significant catalytic impact on lactic acid formation. Nevertheless, Sn²⁺ in aqueous solution hydrolyses and precipitates. Hydrolysis was not suppressed with HCl or H₂SO₄ in the corresponding concentration range.

Table 3 – Catalytic effect of Brønsted acids with multivalent metal ions on lactic acid formation from dihydroxyacetone ($c_{DHA,0} = 0.56 \text{ mol L}^{-1}$, $c_{H^+} = 1 \text{ mol L}^{-1}$, for metal/HCl experiments: $c_{Me} = 0.06 \text{ mol L}^{-1}$, 99 °C, reaction time: 1 h).

acid	Me	$X_{DHA}^{\%}$	$Y_{PA}^{\%}$	$Y_{LA}^{\%}$	$Y_{LA}^{[c]}^{\%}$
HCl	Zn ²⁺	100	70	5	23
HCl	Sn ²⁺	100	≤ 0.1	75	75
HCl	Fe ²⁺	≥ 99.9	84	7	26
HCl	Fe ³⁺	≥ 99.9	77	4	23
HCl	Al ³⁺	≥ 99.9	74	24	51
HCl	Cr ²⁺	≥ 99.9	48	46	91
HCl	Cr ³⁺	≥ 99.9	45	40	91
Lewatit®K2620 ^[a]	Al ³⁺ ^[b]	42	20	8	73
Lewatit®K2620 ^[a]	Cr ³⁺ ^[b]	67	13	31	89

^[a]98 °C ^[b]doped ^[c]reaction time: 6 h

With Al³⁺/HCl, the lactic acid yield was 24 % after one hour, and 51 % after six hours. Al³⁺ had an accelerating effect on lactic acid formation without the negative side effect of precipitation.

Admixture of Zn²⁺, Fe²⁺, and Fe³⁺ had a negative impact on lactic acid formation. Even though, conversion of dihydroxyacetone was comparable for Al³⁺ and Zn²⁺, admixture of Zn²⁺ resulted in increased formation of unidentified by-products. Low yields of pyruvic aldehyde with Zn²⁺ indicated that by-product formation was favoured. Yields of lactic acid were higher with Fe²⁺ than with Fe³⁺ or Zn²⁺.

The highest catalytic effect on lactic acid formation was achieved with Cr²⁺/HCl and Cr³⁺/HCl.

Doping of Lewatit®K2620 with Al³⁺ and Cr³⁺ showed a high catalytic effect on lactic acid formation, too. The lactic acid yields were 73 % and 89 % after six hours with Al³⁺ and Cr³⁺-doped Lewatit®K2620. The yield was limited to 14 % with non-doped Lewatit®K2620. Conversion rates of dihydroxyacetone were lower with both non-doped and doped Lewatit®K2620 with respect to the HCl catalysed reaction. This confirms that dihydroxyacetone dehydration requires strongly acidic reaction conditions, not provided by the specific ion-exchange resin.

The higher yields with Al³⁺-doped Lewatit®K2620 (73 % after six hours) with respect to Al³⁺/HCl (51 %) may be attributed to the higher concentrations of metal ions due to doping. However, reusability of metal-doped Lewatit®K2620 was unsatisfactory. Lactic acid yields after six hours dropped to 61 % after reuse of Al³⁺-doped Lewatit®K2620. Aluminium, detected in the reaction solution, confirmed that the stability of the Al³⁺-laden resin was unsatisfactory. Limited stability of

metal-doped Lewatit®K2620 and toxicity of chromium were unfavourable for Cr^{3+} catalyst.

In Figure 6, dihydroxyacetone conversion, formation of the intermediate pyruvic aldehyde and the product lactic acid are compared for HCl catalysed and HCl/ Al^{3+} catalysed reaction. Dihydroxyacetone conversion was comparable for both catalysts. Admixture of catalytic amounts of Al^{3+} had a high accelerating impact on the rate determining conversion of pyruvic aldehyde. This selective acceleration of lactic acid formation from pyruvic aldehyde may be attributed to chelate complexes formed of pyruvic aldehyde and Al^{3+} .²⁶ Bicker *et al.*²² proposed that an inversion of the polarity of the Lewis acid to a Lewis base for metal ions could occur. The latter is able to form a complex between pyruvic aldehyde and the metal ion. Then rehydration of this complex leads to the formation of lactic acid and the free catalyst.

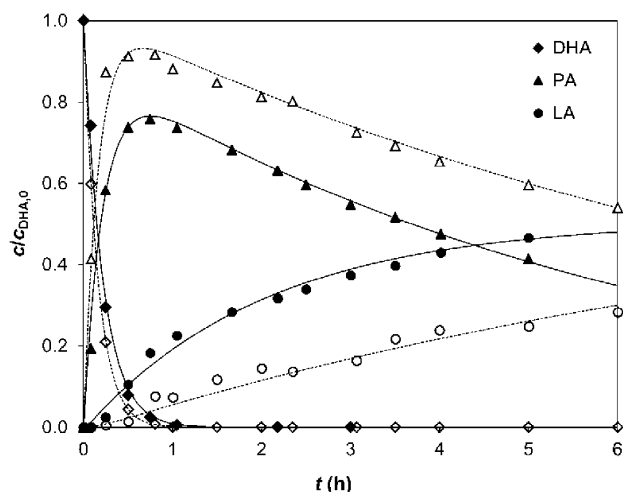


Fig. 6 – Comparison of HCl (blank data points/dashed lines) and HCl plus Al^{3+} (full data points/solid lines) catalysed lactic acid formation from dihydroxyacetone ($c_{\text{DHA},0} = 0.56 \text{ mol L}^{-1}$, $c_{\text{HCl}} = 1 \text{ mol L}^{-1}$, $c_{\text{Al}} = 0.06 \text{ mol L}^{-1}$, 99°C)

Catalysis with metal salts

Comparison of different metal salts

For a catalyst screening, the soluble metal salts $\text{Al}_2(\text{SO}_4)_3$, CuSO_4 , ZnSO_4 , and ZrOCl_2 were compared (Table 4). Experiments were performed with 0.56 mol L^{-1} feed dihydroxyacetone at 99°C .

Whereas $\text{Al}_2(\text{SO}_4)_3$ showed high catalytic activity and selectivity for lactic acid, the selectivity towards lactic acid with ZnSO_4 and ZrOCl_2 was low. The yield of lactic acid after six hours was 54 % with $\text{Al}_2(\text{SO}_4)_3$, compared to 21 % with ZrOCl_2 when a metal ion concentration of 0.06 mol L^{-1} was used. It was 73 % with $\text{Al}_2(\text{SO}_4)_3$ compared to 4 % with ZnSO_4 when stoichiometric metal ion concentration of 0.56 mol L^{-1} was used.

Table 4 – Catalytic effect of various metal salts on lactic acid formation from dihydroxyacetone (reaction time: 1 h; $c_{\text{DHA},0} = c_{\text{Me}} = 0.56 \text{ mol L}^{-1}$, 99°C)

Metal salt	$X_{\text{DHA}}^{\text{DHA}}/\%$	$Y_{\text{PA}}^{\text{PA}}/\%$	$Y_{\text{LA}}^{\text{LA}}/\%$	$Y_{\text{LA}}^{\text{LA}}/[\text{b}]/\%$
$\text{Al}_2(\text{SO}_4)_3$ ^[a]	63	21	22	73
$\text{Al}_2(\text{SO}_4)_3$	97	15	57	77
$\text{Al}(\text{NO}_3)_3$	78	28	50	77
ZnSO_4	87	1	3	4
ZrOCl_2 ^[a]	100	2	18	21
CuSO_4	n.a.	–	–	–

^[a] $c_{\text{Me}} = 0.14 \text{ mol L}^{-1}$ ^[b]reaction time: 6 h

Minor amounts of isomeric glyceraldehyde were detected for aluminium salt catalysts. Glyceraldehyde was not detected with CuSO_4 , ZnSO_4 and ZrOCl_2 .

Even though the use of ZnSO_4 resulted in dihydroxyacetone conversion of more than 85 % after one hour, selectivity for lactic acid remained below 4 %. ZnSO_4 dissolves in aqueous solution under acidic hydrolysis providing acidic media for dihydroxyacetone conversion to pyruvic aldehyde. The fact that pyruvic aldehyde was not detected in remarkable amounts accounts for a fast subsequent reaction. But side reactions were dominating and lactic acid formation was suppressed.

With ZrOCl_2 , dihydroxyacetone was converted within one hour. Lactic acid selectivity remained rather low at 21 %. Since pyruvic aldehyde was not detected in remarkable amounts, again by-product formation could be assumed by the material balance.

Lactic acid was not formed with CuSO_4 .

Catalysis with the Lewis acid aluminium sulphate

With respect to the high catalytic effect, high selectivity for lactic acid and advantageous dissolution properties, further experiments were performed with $\text{Al}_2(\text{SO}_4)_3$ as catalyst.

Two complementary effects are observed with $\text{Al}_2(\text{SO}_4)_3$. Firstly, $\text{Al}_2(\text{SO}_4)_3$ dissolves under strongly acidic hydrolysis providing acidic reaction conditions. High acidity of the aqueous reaction solution is essential for dehydration of dihydroxyacetone to pyruvic aldehyde. Secondly, the multivalent metal ion Al^{3+} catalyses the intramolecular Cannizzaro reaction of pyruvic aldehyde to form lactic acid. This may be attributed to complex formation of the intermediate pyruvic aldehyde and the metal ion. Rehydration of this complex leads to the formation of lactic acid and then the free catalyst. Lactic acid formation from pyruvic aldehyde is rate determining under acid catalysis with HCl (Table 2).

Similar to the aluminium-catalysed formation of hydroxyacetic acid from glyoxal²⁶, lactic acid formation from pyruvic aldehyde is a first order reaction with respect to pyruvic aldehyde. Experiments were performed with pyruvic aldehyde and the reaction kinetics was confirmed.

Representative conversion graphs for the Al^{3+} catalysed reaction of dihydroxyacetone to lactic acid are shown in Figure 7.

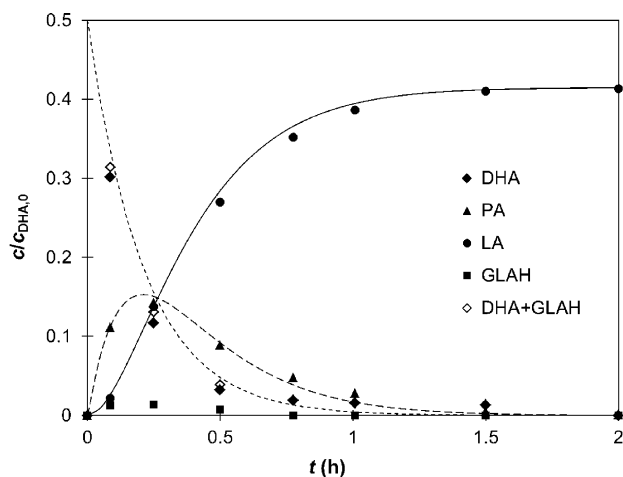


Fig. 7 – Course of dihydroxyacetone, pyruvic aldehyde, glyceraldehyde, and lactic acid concentrations for Al^{3+} catalysed conversion of dihydroxyacetone to lactic acid (catalyst: $\text{Al}_2(\text{SO}_4)_3$, $c_{\text{DHA},0} = 0.56 \text{ mol L}^{-1}$, $c_{\text{Al}} = 0.83 \text{ mol L}^{-1}$, 99°C)

Isomeric glyceraldehyde was detected at the beginning of the reaction. Both dihydroxyacetone and glyceraldehyde contributed to lactic acid formation. Opposite to the HCl -catalysed reaction, dehydration of dihydroxyacetone to pyruvic aldehyde was rate-determining with the catalyst $\text{Al}_2(\text{SO}_4)_3$.

The initially transparent reaction solution changed colour to yellowish and finally dark brown with ongoing reaction time. This was also observed when performing the conversion with the catalyst HCl . Oligo- and polymerization of pyruvic aldehyde and dihydroxyacetone may be indicated as the governing reason for colour change and formation of insoluble by-products.²³

Effect of the reaction temperature

The effect of the reaction temperature on the aluminium-catalysed lactic acid formation was investigated in a temperature range of 70°C to 99°C (reflux boiling conditions) with 0.56 mol L^{-1} feed dihydroxyacetone. The molar ratio of feed Al^{3+} /dihydroxyacetone was 1.

As expected from the HCl -catalysed reaction, lactic acid yields increased with increasing reaction

temperature. Whereas the lactic acid yield after six hours was low (10 %) at 70°C , high yields of 78 % were achieved at reflux boiling conditions (99°C). Complete conversion of dihydroxyacetone was achieved within six hours at 99°C . At 70°C , residual dihydroxyacetone was still 22 % after six hours. At 99°C , maximum yields of pyruvic aldehyde of 30 % after 15 minutes indicated a fast consecutive reaction to lactic acid.

No change in reaction mechanism was indicated from the Arrhenius' plot within the investigated temperature range. Table 5 lists the activation energies E_A and pre-exponential factors A for the first ($\text{DHA} \rightarrow \text{PA}$) and second ($\text{PA} \rightarrow \text{LA}$) reaction step.

Table 5 – Activation energy E_A and pre-exponential factor A for aluminium-catalysed conversion of dihydroxyacetone to lactic acid (catalyst: $\text{Al}_2(\text{SO}_4)_3$, $c_{\text{DHA},0} = c_{\text{Al}} = 0.56 \text{ mol L}^{-1}$)

	$A \text{ (h}^{-1}\text{)}$	$E_A \text{ (kJ mol}^{-1}\text{)}$
1. $\text{DHA} \rightarrow \text{PA}$	$(4.39 \pm 0.01) \cdot 10^{13}$	93.5 ± 0.2
2. $\text{PA} \rightarrow \text{LA}$	$(2.68 \pm 0.01) \cdot 10^{12}$	91.8 ± 0.2

Effect of aluminium sulphate concentration

The effect of the $\text{Al}_2(\text{SO}_4)_3$ concentration on the rate of conversion was investigated by variation of the molar ratio of Al^{3+} to dihydroxyacetone from 0.01 to 1.5. Feed concentration of dihydroxyacetone was 0.56 mol L^{-1} in the experiments. As expected, increasing Al^{3+} concentration resulted in the acceleration of lactic acid formation. Figure 8 shows the lactic acid yields for varying Al^{3+} /dihydroxyacetone feed ratio. The maximum lactic acid yield was 73 %. No difference in selectivity towards pyruvic aldehyde and lactic acid was observed for varying Al^{3+} concentration of 0.006 to 0.83 mol L^{-1} .

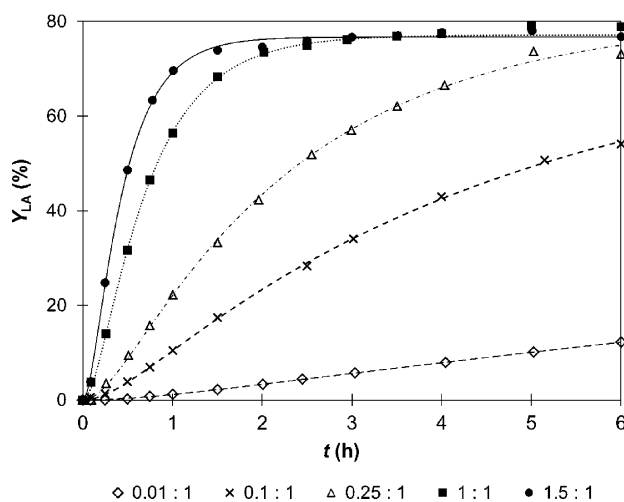


Fig. 8 – Effect of the molar feed ratio Al^{3+} /dihydroxyacetone on the formation of lactic acid from dihydroxyacetone (catalyst: $\text{Al}_2(\text{SO}_4)_3$, $c_{\text{DHA},0} = 0.56 \text{ mol L}^{-1}$, 99°C)

Rate constants k_1 and k_2 for different $\text{Al}_2(\text{SO}_4)_3$ concentrations are given in Table 6. An almost linear correlation between k_1 and k_2 and the $\text{Al}_2(\text{SO}_4)_3$ concentration was observed. With increasing $\text{Al}_2(\text{SO}_4)_3$ concentration, the difference between k_1 and k_2 reduced. This may be explained by increasing acidity of the solution resulting from high $\text{Al}_2(\text{SO}_4)_3$ concentrations.

Table 6 – Rate constants k_1 and k_2 of the aluminium-catalysed conversion of dihydroxyacetone to lactic acid (catalyst: $\text{Al}_2(\text{SO}_4)_3$, $c_{\text{DHA},0} = 0.56 \text{ mol L}^{-1}$, 99°C)

c_{Al} (mol L^{-1})	k_1 (h^{-1})	k_2 (h^{-1})
0.006	0.10	0.30
0.056	0.42	0.94
0.14	0.89	1.2
0.56	3.1	3.2
0.84	4.7	4.8

Conclusions

Synthesis of lactic acid from aqueous dihydroxyacetone solution is a promising approach for chemical production from bio-based precursors. Handling of aqueous reaction systems and integrated approaches including product separation are of prime importance for exploitation of biomass. Catalysis of the liquid phase reaction was investigated with Brønsted acids, acidic hydrolysing metal salts, and a combination thereof. Brønsted acids are often present in aqueous solutions of bio-based precursors.

Lactic acid formation favours high temperatures and strongly acidic operating conditions. Lactic acid yields of 83 % were achieved when carrying out the reaction under reflux boiling conditions and the catalyst HCl in excess. Lactic acid formation from dihydroxyacetone proceeds via two consecutive reaction steps with pyruvic aldehyde serving as intermediate. Conversion of pyruvic aldehyde is rate controlling under acid catalysis. The rate of pyruvic aldehyde conversion is accelerated with catalytic amounts of multivalent Al^{3+} and Sn^{2+} . The Lewis acid $\text{Al}_2(\text{SO}_4)_3$ provides both acidic reaction conditions for dehydration of dihydroxyacetone to pyruvic aldehyde and acceleration of lactic acid formation from pyruvic aldehyde. Both acid and Al^{3+} catalysis is promising for the synthesis of lactic acid from aqueous dihydroxyacetone solutions.

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Nomenclature

- A – pre-exponential factor, h^{-1}
 c – concentration, mol L^{-1}
 X – conversion, %
DHA – dihydroxyacetone
 E_A – activation energy, kJ mol^{-1}
 k – rate constant, h^{-1}
LA – lactic acid
Me – metal
PA – pyruvic aldehyde
 S – selectivity
 t – time, h
 Y – yield, %

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