CHEMSUSCHEM

DOI: 10.1002/cssc.201000457

# Catalytic Conversion of Dihydroxyacetone to Lactic Acid Using Metal Salts in Water

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We herein present a study on the application of homogeneous catalysts in the form of metal salts on the conversion of trioses, such as dihydroxyacetone (DHA), and glyceraldehyde (GLY) to lactic acid (LA) in water. A wide range of metal salts (26 in total) were examined. $Al^{III}$ salts were identified as the most promising and essentially quantitative LA yields (>90 mol%) were obtained at 140 °C and a reaction time of 90 min. A reaction pathway is proposed and a kinetic model using the power law approach was developed for the conversion of DHA to LA with pyruvaldehyde (PRV) as the intermediate. Good agreement between experimental data and the model was obtained. Model predictions, supported by experiments, indicate that a high yield of LA is favoured in dilute solutions of DHA (0.1 M) at elevated temperatures (180 °C) and reaction times less than 10 min.

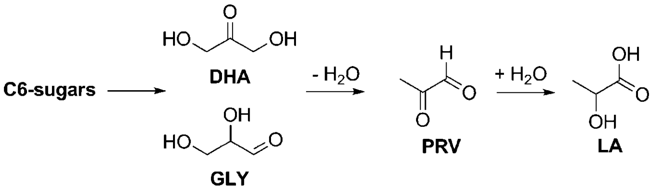
## Introduction

High oil prices and environmental concerns have stimulated research on biofuels and biobased chemicals from lignocellulosic biomass. Attractive catalytic conversions to platform chemicals have been identified[1] and activities are ongoing to convert these findings to economically feasible processes on a large scale.[2] Examples of interesting platform chemicals are organic acids, such as levulinic acid, propionic acid, acrylic acid and, in particular, lactic acid (LA).

LA is a commodity chemical with an estimated demand of 300000 tonnes per year (2010).[3] Traditionally, LA is used in food and food-related applications, such as bakery and meat products and confectionery.[3] In these applications, LA serves as a pH regulator, as a preservative or as an emulsifying agent. LA is also used for non-food applications and examples are found in cosmetic and pharmaceutical formulations.[3] In the last decade, the commercialisation of polylactic acid (PLA), which is a biopolymer with interesting applications, has boosted the production of LA considerably. Market projections indicate that the PLA market may reach up to 3 million tonnes in 2020.[4] Furthermore, LA also has potential as a platform chemical for the production of bulk chemicals, such as propylene glycol and acrylic acid.[5]

LA is currently produced by fermentation processes using carbohydrate sources. However, volumetric production rates are relatively low and product workup leads to the formation of large amounts of salts.[3,6] Therefore, novel methods to produce LA from lignocellulosic biomass through non-fermentative catalytic chemical transformations have attracted great interest in both academia and industry.

A number of studies have been reported in the literature and involve the use of C6 sugars (D-glucose and D-fructose),[7] C6 sugar precursors, such as cellulose,[7c] and trioses,[7a,g,8] such as dihydroxyacetone (DHA) and glyceraldehyde (GLY), as the feedstock. The reactions with C6 sugars or C6 sugar precursors are typically performed in subcritical water ($T > 250$ °C) in the presence of homogenous catalysts, such as bases (NaOH and $Ca(OH)_2$)[7b,e] or metal salts.[7a,c,g,8a] However, the reported yields of LA are relatively low (<45 mol%). Interestingly, these studies imply that trioses, such as DHA, GLY, as well as pyruvaldehyde (PRV), are intermediates when converting C6 sugars into LA (Scheme 1).



Scheme 1. Conversion of C6 sugars to LA.

These findings stimulated research activities on the conversion of trioses, such as DHA and GLY, into LA. Homo- and heterogeneous catalysts have been explored, mainly in protic solvents, such as water and alcohols (methanol and ethanol), and an overview is given in Table 1. When using dilute sulfuric acid as the catalyst in subcritical water (250 °C, 24.5 MPa), Antal et al. observed the formation of LA in low yields (15 mol%; Table 1, entry 1).[8a] Bicker et al. reported catalytic effects of var-

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**Table 1.** Overview of catalytic conversions of DHA to LA or alkyl lactates.

| Entry | Solvent | [DHA] | Catalyst | Metal/DHA ratio [mol%] | Conditions | Conversion | Yield [mol%] | Ref. |
|---|---|---|---|---|---|---|---|---|
| 1 | $H_2O$ | 0.1 M | $H_2SO_4$ (1 mM) | – | 250 °C, 24.5 MPa, 33 s | 75 | 15[a] | [8a] |
| 2 | $H_2O$ | 1 wt% | $ZnSO_4$ (400 ppm) | 2.2 | 300 °C, 25 MPa, 30 s | – | 86[b] | [7a] |
| 3 | $H_2O$ | 0.1 M | $AlCl_3·6H_2O$ (5 mM) | 5 | 140 °C, 90 min | 100 | 90[a] | [7g] |
| 4 | $H_2O$ | 40 wt% | Cr resin | 0.2–5[d] | 100 °C, 5 h | 100 | 86[a] | |
| 5 | $H_2O$ | 40 wt% | Sn resin | 0.2–5[d] | 100 °C, 5 h | 100 | 68[a] | [8b] |
| 6 | $H_2O$ | 40 wt% | Al resin | 0.2–5[d] | 100 °C, 5 h | 100 | 42[a] | |
| 7 | $H_2O$ | 0.25 M | Sn-beta zeolite (80 mg, Si/Sn = 125) | – | 125 °C, 24 h | 100 | 90[a] | [8f] |
| 8 | $H_2O$ | 0.31 M | H-USY zeolite (80 mg, Si/Al = 6) | – | 125 °C, 24 h | 99 | 71[a] | [8h] |
| 9 | MeOH | 0.625 M | $SnCl_2$ (62.5 mM) | 10 | 90 °C, 3 h | – | 89[c] | |
| 10 | MeOH | 0.625 M | $CrCl_3·6H_2O$ (62.5 mM) | 10 | 90 °C, 3 h | – | 50[c] | [8e] |
| 11 | MeOH | 0.625 M | $AlCl_3·6H_2O$ (62.5 mM) | 10 | 90 °C, 3 h | – | 62[c] | |
| 12 | MeOH | 0.25 M | Sn-beta zeolite (80 mg, Si/Sn = 125) | – | 80 °C, 24 h | 100 | 99[c] | [8f] |
| 13 | EtOH | 0.4 M | USY-CBV 600 zeolite (200 mg, SI/Al = 2.6) | – | 90 °C, 6 h | 77 | 59[c] | [8g] |
| 14 | MeOH | 0.25 M | H-USY zeolite (80 mg, Si/Al = 6) | – | 105 °C, 24 h | 99 | 96[c] | [8h] |

[a] Yield of LA. [b] Selectivity of LA. [c] Yield of alkyl lactate. [d] Expressed as the ratio of the amount of transition metal and intake of reactant (mol/mol).

ious metal ions ($Co^{II}$, $Ni^{II}$, $Cu^{II}$ and $Zn^{II}$) on the conversion of DHA in subcritical water to LA, and $Zn^{II}$ gave the best results regarding LA selectivity (86 mol%, conversion data not given; Table 1, entry 2).[7a] We recently discovered that $Al^{III}$ salts gave a high yield of LA (90 mol%, 90 min reaction time) in water under much milder conditions (140 °C) (Table 1, entry 3).[7g]

The use of heterogeneous catalysts in water has also been explored. Kelly evaluated the application of ion-exchange resins as catalysts for the conversion of DHA to LA under mild conditions (100 °C).[8b] Among the resins tested, Cr-containing resins gave the highest LA yield (86 mol%; Table 1, entry 4). While performing this study, the application of a Sn-beta zeolite[8f] and an ultrastable-Y zeolite (H-USY)[8h] on the conversion of DHA to LA was reported. High yields of LA (up to 90 mol%) were achieved at 125 °C for both types of zeolites, though long reaction times up to 24 h were required (Table 1, entries 7 and 8).

Several authors reported the use of alcohols as solvents in combination with homo- and heterogeneous catalysts for the synthesis of alkyl lactates from trioses. Hayashi and Sasaki demonstrated that tin chloride was a highly selective catalyst for the reaction and methyl lactate was obtained at 89 mol% yield when reacting DHA (0.625 M) in methanol using 10 mol% $SnCl_2$ (3 h, 90 °C; Table 1, entry 9).[8e] Taarning and co-workers reported that heterogeneous Sn-based catalysts (Sn-beta zeolite) were also suitable catalysts for the conversion of hexoses or trioses to methyl lactate in methanol.[7f,8f] A high yield of methyl lactate (99 mol%) was obtained when using DHA, although relatively long reaction times of up to 24 h were required (Table 1, entry 12).[8f] The application of commercial zeolites for the conversion of trioses to alkyl lactate has also been reported.[8g,h] For instance, Pescarmona et al.[8g] and West et al.[8h] studied the use of ultrastable Y (USY) zeolites for the conversion of trioses to alkyl lactates (Table 1, entries 13 and 14). Both studies highlight the importance of Lewis acid sites on the zeolite to achieve a high yield of either LA or alkyl lactates.

The metal-catalysed studies discussed above indicate that metal cations, either in solution or in heterogeneous form, catalyse the reactions of trioses to LA. However, exploratory screening studies aimed at the identification of the most promising metals and a better understanding of the reaction pathways are lacking. We herein report our studies on the catalytic effect of a wide range of homogeneous catalysts in the form of metal salts on the conversion of DHA and GLY to LA in aqueous solutions. On the basis of this study, the most promising metal salts were identified and the yields were optimised by variation of process conditions. In addition, a reaction pathway is postulated and supported by kinetic studies.

## Results and Discussion

### Conversion of DHA to LA using homogeneous catalysts

A wide range of homogeneous catalysts in the form of metal salts were tested for the conversion of DHA to LA in water. The reactions were performed in glass ampoules at a temperature of 140 °C using 0.1 M solutions of DHA containing 5 mM metal salt as the catalyst. All reactions were carried out at least in duplicate and show good reproducibility. The conversions of DHA after 90 min reaction time are presented in Figure 1. The selectivity to LA ($S_{LA}$) and PRV ($S_{PRV}$) for all reactions is given in Figure 2. Herein, the selectivities are defined by Equations (1) and (2):

$$S_{LA} = \frac{[LA]}{[DHA]_0 - [DHA]} \times 100\,\% \tag{1}$$

$$S_{PRV} = \frac{[PRV]}{[DHA]_0 - [DHA]} \times 100\,\% \tag{2}$$

in which [LA], [PRV] and [DHA] are the concentrations of LA, PRV and DHA after a certain reaction time, respectively, and $[DHA]_0$ denotes the initial concentration of DHA.

For comparison, the reactions were initially carried out in the absence of a catalyst (thermal) and using Brønsted acids, such as HCl and $H_2SO_4$. The conversion of DHA was 55 mol% for the thermal reaction and >90 mol% when using Brønsted

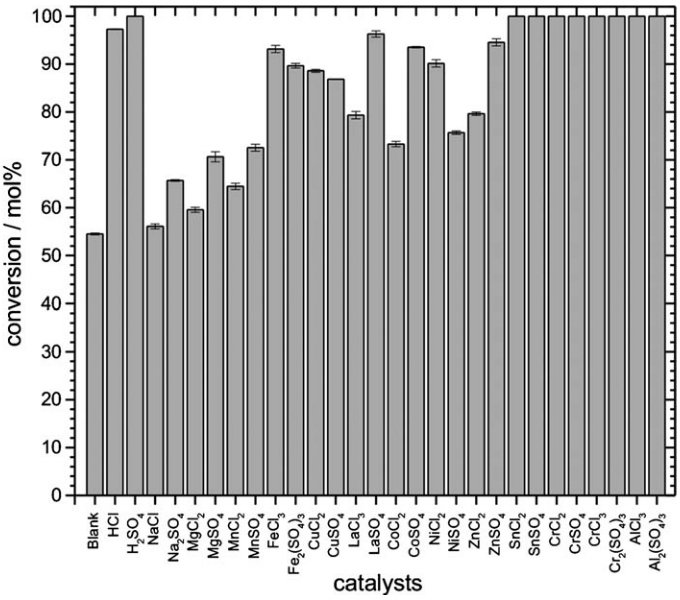


**Figure 1.** Conversion of DHA for various catalysts ($[DHA]_0 = 0.1$ M; [salt] = 5 mM; $T = 140\,^{\circ}C$; $t = 90$ min).

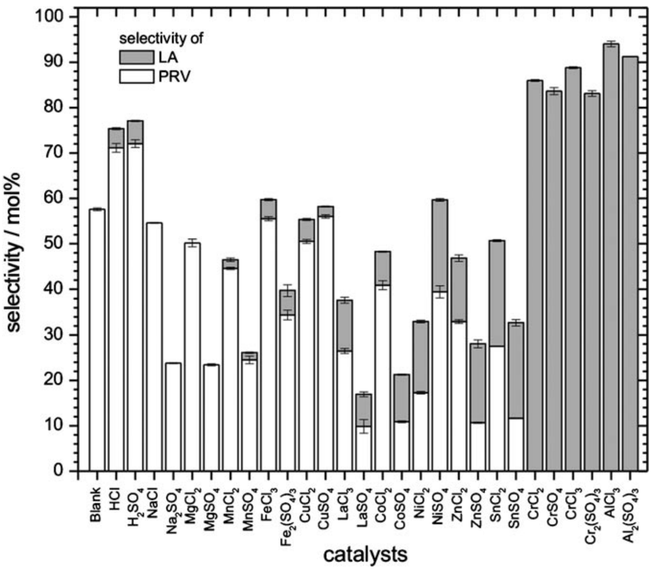


**Figure 2.** Selectivity of PRV ($S_{PRV}$) and LA ($S_{LA}$) for various catalysts ($[DHA]_0 = 0.1$ M; [salt] = 5 mM; $T = 140\,^{\circ}C$; $t = 90$ min).

acids. These results imply that $H^+$ ions have a positive effect on the conversion of DHA. In the absence of catalysts, PRV is the sole product, whereas mixtures of PRV and LA were observed for the Brønsted acids (Figure 2). The major product for Brønsted acids was PRV, and LA was only obtained in low yields (<4 mol%). In addition, brown soluble and insoluble products were observed for both the thermal and Brønsted acid catalysed reactions under these conditions. These results indicate that dehydration of DHA to PRV is the dominant pathway for the thermal and Brønsted acid catalysed reaction (Scheme 1).

Of all 26 metal salts tested, Cr, Al and Sn salts were the most active and gave quantitative conversion of DHA under the conditions employed (Figure 1). However, remarkable differences for the three metals were observed regarding chemoselectivity. When using Al and Cr salts, the selectivity for LA was very high and between 80–92% (Figure 2). The highest selectivity of LA was found for $AlCl_3$. The formation of brown insoluble solids was not observed. On the contrary, the selectivity for Sn salts was always below 25%, making this a less attractive catalyst. In this case, considerable amounts of dark brown insoluble products were observed.

When using metal salts, Brønsted acid catalysis may also play a role because the pH values of aqueous solutions of the best catalysts, $CrCl_3$ and $AlCl_3$ salts, were 2.62 and 3.24, respectively, at room temperature. Thus, one could argue that the good yields of LA for these salts were a result of Brønsted acid catalysis. However, the activity of Brønsted acids such as HCl and $H_2SO_4$ is much lower than that of the Cr and Al solutions (Figure 1); a clear indication that metal cations indeed show catalytic activity. In addition, the chemoselectivity is altered dramatically when using metal salts (Figure 2), from mainly PRV for Brønsted acids to solely LA for Al and Cr salts. Thus, the Al and Cr cations both have a positive effect on activity and chemoselectivity and play a key role in the reaction pathways leading to LA.

When comparing the chemoselectivity for all metal salts, it is evident that Al and Cr are special and produce selectively LA. One possible explanation is that these metal ions catalyse the conversion of the intermediate PRV to LA very efficiently (Scheme 1). To test this hypothesis, the performance of a range of metal salts for the conversion of PRV to LA was evaluated. The reactions were carried out by using a 0.1 M PRV solution containing 5 mM of catalyst at 140 °C for a reaction time of 30 min. The conversion of PRV and the yield of LA are provided in Figure 3. Cr and Al salts are very active and quantitative conversion to LA was observed. For all other salts, the conversion and the yield of LA were much lower (<30 mol%) and brown insoluble products were formed as well. The results indicate

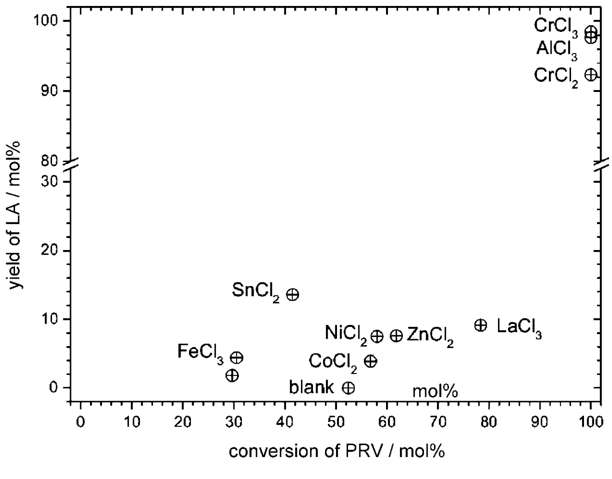


**Figure 3.** Conversion of PRV versus yield of LA for various catalysts ($[PRV]_0 = 0.1$ M; [salt] = 5 mM; $T = 140\,^{\circ}C$; $t = 30$ min).

that the Al and Cr salts effectively catalyse the conversion of the intermediate PRV to LA in aqueous solutions and this is likely to be the explanation for the special role of $Al^{3+}$ and $Cr^{3+}$ for the conversion of trioses to LA.

The main product for the less active metals was a brown solid. It is likely that the source of these insoluble products is PRV, which is known to polymerise at elevated temperatures in aqueous solutions and forms brown insoluble products.[8a] This was tested separately by performing an experiment with PRV in the absence of a catalyst (blank in Figure 3). The PRV conversion was about 52 mol %, whereas brown insoluble products were the sole product, confirming that PRV was a source for the formation of insoluble, polymeric materials.

The starting triose (DHA) may also be involved in the formation of brown insoluble products. This is evident when performing reactions of DHA in the absence of catalysts or when using Brønsted acids; this gives significant amounts of solids. The possible involvement of DHA on the formation of insoluble materials was supported by kinetic modelling results (see below).

Anion effects on the conversion of DHA to LA were explored by performing experiments with Al salts containing different anions. The experiments were performed by using a 0.1 M solution of DHA containing 5 mM of Al salts, and the conversion of DHA and yield of LA after 15 min were determined (Table 2).

**Table 2.** Effect of various anions for Al salts for the reaction of DHA in aqueous solutions ($[DHA]_0 = 0.1$ M, $[salt] = 5$ mM, $T = 140\,°C$, $t = 15$ min).

| Entry | Catalyst | DHA conversion [mol %] | Yield [mol %] GLY | PRV | LA |
|---|---|---|---|---|---|
| 1 | – | 9 | – | 8 | – |
| 2 | $AlCl_3$ | 44 | 3 | 12 | 28 |
| 3 | $Al_2(SO_4)_3$ | 44 | 3 | 17 | 21 |
| 4 | $Al(NO_3)_3$ | 44 | 2 | 12 | 27 |
| 5 | $Al(OTf)_3$ | 43 | 2 | 12 | 26 |

Relatively short reaction times were applied to avoid quantitative conversion of DHA, allowing a proper comparison of catalytic effects. Under these conditions, both LA and the intermediate PRV were present after the reaction. In addition, glyceraldehyde (GLY) was also present in the reaction mixture. The latter is a known isomerisation product of DHA (see below). No major differences were observed for both catalyst activity and product selectivity, suggesting that anion effects were less important in the catalytic pathways.

## Effect of process conditions for the Al-catalysed reaction of DHA to LA

In the screening studies, Al and Cr salts were identified as most promising for the conversion of DHA to LA in aqueous solutions. Due to the fact that Al is less expensive and more non-toxic than Cr, Al salts were selected for further focused studies on the conversion of DHA to LA.

A series of experiments were carried out in a temperature window of 120–180 °C, initial concentrations of DHA between 0.1–1 M, and $AlCl_3$ concentrations ranging from 5 to 10 mM. The product composition at various reaction times was determined. The effect of $AlCl_3$ concentration on the conversion of DHA and yield of LA is presented in Figure 4. Evidently, higher catalyst concentrations lead to higher rates. At the same DHA conversion, the yield of LA is slightly higher when using higher catalyst concentrations.

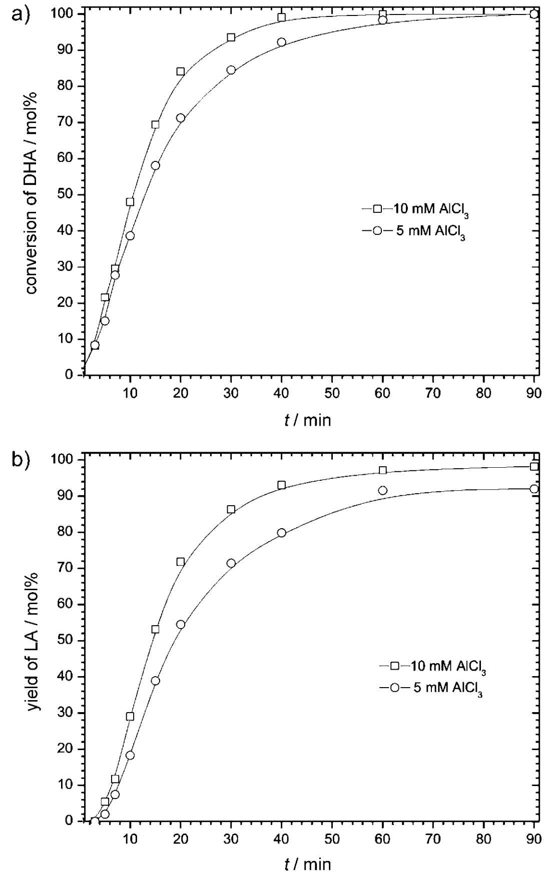


**Figure 4.** Effect of $AlCl_3$ concentration (5 (○) and 10 mM (□)) on the conversion of DHA and yield of LA ($[DHA]_0 = 0.1$ M, $T = 140\,°C$).

The conversion of DHA is a strong function of reaction temperature (Figure 5). Essential quantitative conversions of DHA were achieved within 10 min at the highest temperature in the range (180 °C). At lower temperatures, the rate was reduced considerably and, for instance, a reaction time of 2 h was required for 90 % DHA conversion at 120 °C. The yield of LA shows small, though significant, temperature dependence (Figure 5 b). Highest LA yields (> 90 mol %) were observed at 180 °C.

The effect of initial DHA concentration on the DHA conversion is presented in Figure 6. The DHA conversion is independent of the initial concentration of DHA; an indication that reaction is first order in DHA. However, the yield of LA is a function of the initial concentration of DHA and was significantly higher when using a low initial concentration of DHA (94 vs.

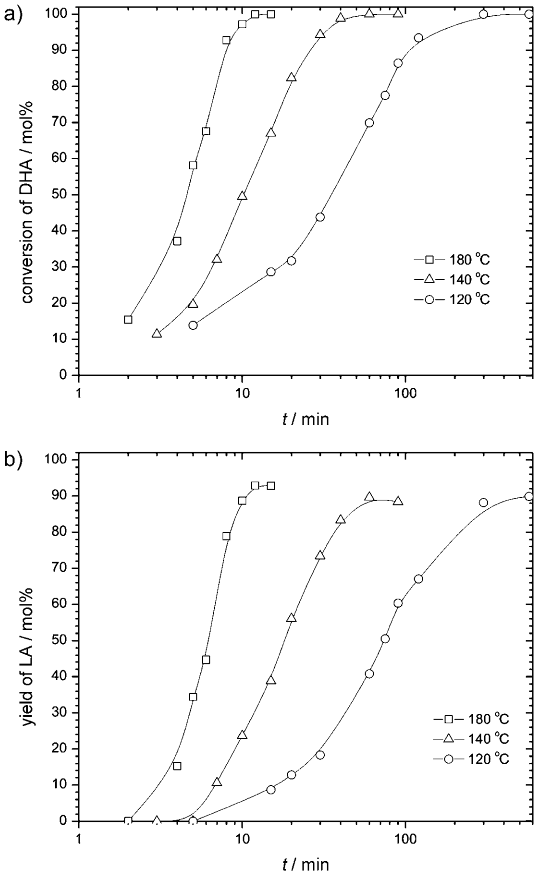


**Figure 5.** Effect of reaction temperature (120 (○), 140 (△) and 180 °C (□)) on the conversion of DHA (a) and yield of LA (b) ($[DHA]_0 = 0.5$ M, $[AlCl_3] = 10$ mM).

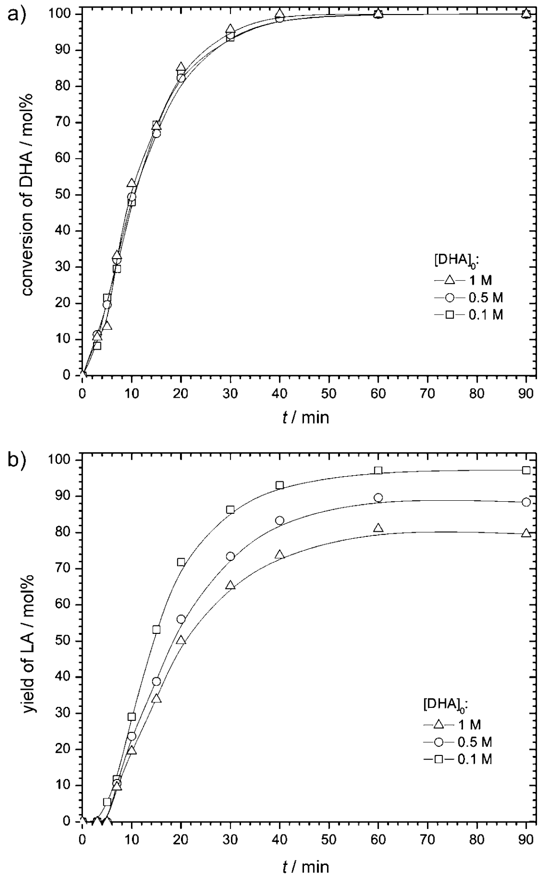


**Figure 6.** Effect of $[DHA]_0$ (0.1 (□), 0.5 (○) and 1 M (△)) on the conversion of DHA and the yield of LA ($[AlCl_3] = 10$ mM, $T = 140$ °C)

80 mol%). The formation of brown soluble materials was observed when using high initial concentrations of DHA; an indication that the side reactions leading to insoluble products have a higher reaction order than the preferred reactions to form LA.

### Determination of reaction pathways

To gain insights in the reaction pathway from DHA to LA, additional experiments were performed with $AlCl_3$ as the catalyst using DHA and GLY as starting materials at an intermediate temperature (140 °C) and variable reaction times. Reactions with GLY were also performed because it is a known isomerisation product of DHA and may play a role in the reaction sequence.[9] A number of representative concentration profiles are presented in Figure 7.

When starting with DHA (Figure 7a), two products were observed, PRV and LA. PRV is an intermediate product and shows a clear optimum, in line with a consecutive reaction pathway. When starting with GLY (Figure 7b), a rapid drop in the concentration of GLY is observed with the concomitant formation of DHA and PRV. At longer reaction times, DHA and PRV react further to give LA.

Based on these observations, a reaction sequence for the conversion of trioses (DHA and GLY) to LA is proposed and given in Scheme 2. In the case of GLY as a starting material, GLY initially isomerises to form DHA.[8h, 9] The subsequent reaction of DHA to LA involves two steps with PRV as the intermediate. The first step in the sequence (DHA to PRV) is likely to involve a keto–enol tautomerisation followed by dehydration to the enol form of PRV. Subsequent tautomerisation then leads to PRV. The conversion of PRV to LA may proceed by a hydration–rearrangement step. The source of the insoluble byproducts are PRV and DHA (see below), most likely by oligo- and polymerisation reactions.

Catalytic effects of $Al^{3+}$ (and $Cr^{3+}$) cations were observed for both the overall reaction of DHA to LA (Figure 1) and the conversion of PRV to LA (Figure 3). For the reaction of DHA to PRV, it is likely that the cations act as Lewis acid catalysts and accelerate the keto–enol tautomerisation and subsequent dehydration by coordination to the carbonyl and hydroxyl groups. This mechanism was also proposed for the tin-catalysed conversion of DHA in alcohols to alkyl lactate.[8e] Besides catalytic effects of the metal ion, the conversion of DHA to PRV is also catalysed by $H^+$, as shown for the reaction of DHA using mineral acids (Figure 1).

The reaction of the intermediate PRV to LA was shown to be catalysed by Al and Cr ions only and as such these two metals

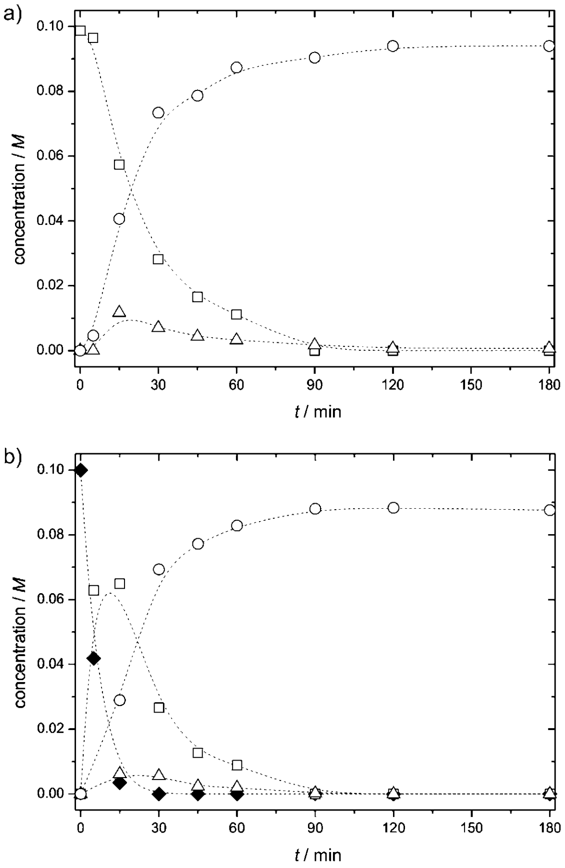


**Figure 7.** Concentration profiles for the reaction of DHA (□) and GLY (◆) using $AlCl_3$ as the catalyst to form PRV (△) and LA (○) ($[AlCl_3] = 5$ mM, $T = 140$ °C)

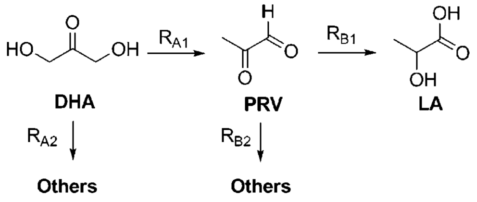
are unique. The reaction is likely to involve hydration followed by a 1,2-hydride shift.[8e] The metal ions act as Lewis acid catalysts by coordination and activation of the carbonyl group. Without further experimentation (e.g., solution studies on the coordination chemistry of $Al^{3+}$ with PRV, X-ray diffraction studies on isolated compounds and theoretical studies), it is not possible to answer the question why $Al^{3+}$ (and $Cr^{3+}$) are unique for the reaction and why other metals tested are far less active and selective.

### Kinetic modelling: Model development

A kinetic model for the reaction of DHA to LA in water was developed by using $AlCl_3$ as the catalyst. It involves the main reactions as well as possible side reactions to insoluble products. It is based on the following considerations:

The reaction rate equations are quantified by using the power law approach instead of a pseudo-first-order approach.

The first step in the reaction is the conversion of DHA to PRV (see Scheme 3). The rate of this reaction is expressed by Equations (3) and (4), in which $T_r$ is the reference temperature (140 °C):



**Scheme 3.** Proposed kinetic scheme for the conversion of DHA to LA.

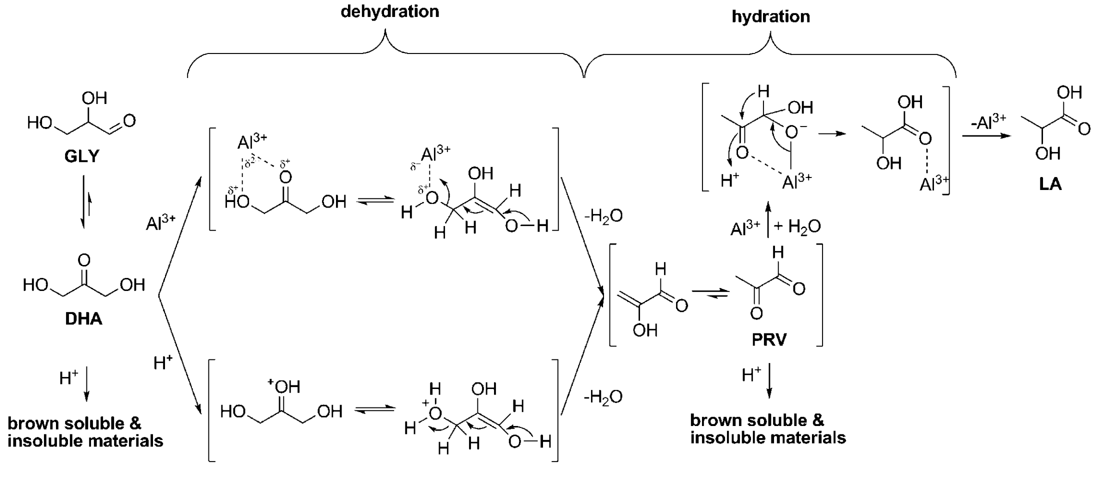
$$R_{A1} = k_{R_{A1}}[DHA]^{\alpha} \tag{3}$$

$$k_{R_{A1}} = k_{R_1} \exp\left[-\frac{E_{R_{A1}}}{R}\left(\frac{1}{T} - \frac{1}{T_r}\right)\right] \tag{4}$$

The involvement of DHA in the formation of insoluble byproducts is described by Equations (5) and (6):

$$R_{A2} = k_{R_{A2}}[DHA]^{\beta} \tag{5}$$

$$k_{R_{A2}} = k_{R_2} \exp\left[-\frac{E_{RA2}}{R}\left(\frac{1}{T} - \frac{1}{T_r}\right)\right] \tag{6}$$



**Scheme 2.** Possible reaction pathway for the conversion of trioses to LA in aqueous solutions by using $Al^{III}$ salts as the catalyst.

The reaction of PRV to LA (Scheme 3) is expressed by Equations (7) and (8):

$$R_{B1} = k_{R_{B1}}[PRV]^{\gamma} \tag{7}$$

$$k_{R_{B1}} = k_{R_3}\exp\left[-\frac{E_{R_{B1}}}{R}\left(\frac{1}{T}-\frac{1}{T_r}\right)\right] \tag{8}$$

The conversion of PRV to insoluble byproducts is quantified by using Equations (9) and (10):

$$R_{B2} = k_{R_{B2}}[PRV]^{\delta} \tag{9}$$

$$k_{R_{B2}} = k_{R_4}\exp\left[-\frac{E_{RB2}}{R}\left(\frac{1}{T}-\frac{1}{T_r}\right)\right] \tag{10}$$

The isomerisation of DHA to GLY was not taken into account. When using DHA as the starting material, GLY was observed only in very minor amounts in the initial stages of the reaction, which made it difficult to determine its concentration accurately.

The experiments were carried out at a fixed $AlCl_3$ concentration of 10 mᴍ and as such the catalyst concentration was not taken into account in the modelling study.

To investigate the possible autocatalytic effect of LA, additional experiments were performed in the presence of LA (0.2 ᴍ DHA, 10 mᴍ $AlCl_3$, 0.2 ᴍ LA). The results were compared with a series of experiments without LA addition at the start of the reaction (blank). The reactions were performed at 140 °C and the results are depicted in Figure 8. Significant effects of the addition of LA on the conversion of DHA and yield of LA (Figure 8) are absent, even though the acidity of the initial reaction mixture with 0.2 ᴍ LA present is higher (pH 2.27) than the blank solution (pH 3.48). We may thus conclude that LA is by far less active than Al species and that autocatalytic effects due to formation of LA are absent under the prevailing conditions.

For a batch reactor setup, the concentrations of the individual species as a function of time using the proposed kinetic model in Scheme 3 may be represented by the ordinary differential Equations (11)–(13):

$$\frac{d[DHA]}{dt} = -R_{A1} - R_{A2} \tag{11}$$

$$\frac{d[PRV]}{dt} = R_{A1} - R_{B1} - R_{B2} \tag{12}$$

$$\frac{d[LA]}{dt} = R_{B1} \tag{13}$$

The kinetic experiments were carried out in glass ampoules placed in an oven and rapidly heated up to reaction temperature. To compensate for non-isothermal behaviour at the start of the reaction, the temperature profile during heating up was determined experimentally by performing experiments with pure water. The resulting equation for the heating up profile was also included in the kinetic model to compensate for non-isothermal behaviour at the initial phase of the reaction.[10]

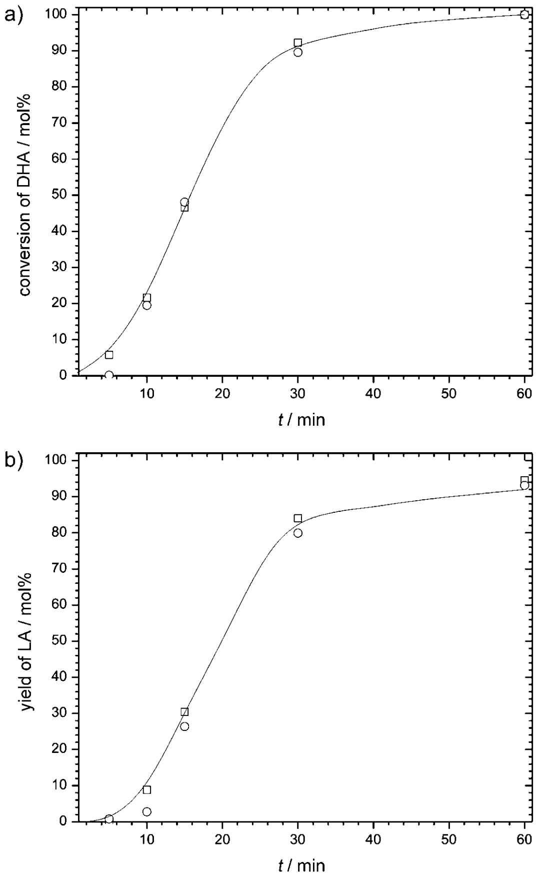


**Figure 8.** DHA conversion and LA yield as a function of time for experiments in the presence (□) and absence of LA (○) at the start of the reaction ($[DHA]_0 = 0.2$ ᴍ, $[AlCl_3] = 10$ mᴍ, $T = 140$ °C).

The rate expressions [Eqs. (3)–(10)] in combination with the mass balances [Eqs. (11)–(13)] and temperature profile in the initial stage of the reaction were applied to model the experimental batch data.

The kinetic modelling activities were performed in two distinct stages. Initially experiments were carried out and modelled by using PRV as the starting material to gain insights in the reaction rates of PRV to LA and insoluble products (reactions $R_{B1}$ and $R_{B2}$). In the second stage, reactions were carried out by using DHA as the starting material. The experiments in the second stage were modelled by using kinetic input from the first stage to obtain the kinetic data for the reaction of DHA to PRV (reactions $R_{A1}$ and $R_{A2}$).

A total of nine batch experiments were performed for stage one of the kinetic study involving the reaction of PRV to LA and solid byproducts. Each experiment provided concentration profiles of reactants and soluble products as a function of time. A temperature window of 120–180 °C, initial PRV concentrations between 0.1–0.5 ᴍ and a fixed $AlCl_3$ intake of 10 mᴍ were applied. A total of 11 batch experiments were performed for stage 2, using initial concentrations of DHA between 0.1–1 ᴍ and a similar temperature window and catalyst intake as those used for stage 1.

The kinetic parameters were estimated by minimising the errors between experimental data and the kinetic model. The best estimates of the kinetic parameters and their standard deviation were determined by using a MATLAB optimisation routine (lsqnonlin), and the results are presented in Table 3.

**Table 3.** Kinetic parameters for the conversion of DHA and PRV to LA using 10 mM $AlCl_3$ as the catalysts.

| Parameter | Value[a] |
|---|---|
| $R_{A1}$ and $R_{A2}$ | |
| $\alpha$ | $0.97 \pm 0.04$ |
| $\beta$ | $1.08 \pm 0.18$ |
| $k_{R_1}$ [$M^{1-\alpha}$ $min^{-1}$][a] | $0.075 \pm 0.006$ |
| $k_{R_{A2}}$ [$M^{1-\beta}$ $min^{-1}$][a] | $0.008 \pm 0.002$ |
| $E_{R_{A1}}$ [kJ $mol^{-1}$] | $93 \pm 3$ |
| $E_{R_{A2}}$ [kJ $mol^{-1}$] | $58 \pm 14$ |
| $R_{B1}$ and $R_{B2}$ | |
| $\gamma$ | $0.73 \pm 0.02$ |
| $\delta$ | $1.30 \pm 0.18$ |
| $k_{R_3}$ [$M^{1-\gamma}$ $min^{-1}$][a] | $0.105 \pm 0.005$ |
| $k_{R_4}$ [$M^{1-\delta}$ $min^{-1}$][a] | $0.022 \pm 0.005$ |
| $E_{R_{B1}}$ [kJ $mol^{-1}$] | $68 \pm 3$ |
| $E_{R_{B2}}$ [kJ $mol^{-1}$] | $72 \pm 15$ |

[a] The values were determined at $T_r = 140\,^{\circ}C$.

A good fit between experimental data and model was obtained, as shown for a number of representative experiments in Figure 9. A parity plot in Figure 10 also illustrates the goodness of fit between the experimental data and model.

In the proposed kinetic scheme, DHA reacts to form PRV ($R_{A1}$) and oligo-/polymeric products ($R_{A2}$). The data were also modelled by using a simplified reaction scheme without the involvement of $R_{A2}$, and as such following a reaction scheme proposed by West et al.[8h] for the conversion of DHA to LA by using USY zeolites as catalysts. To compare the quality of the models, both the coefficient of determination ($R^2$) and Akaike's information criterion (AIC) were used (Table 4). The best model yields to high $R^2$ and a low AIC value. It is evident that model including $R_{A2}$ has a higher value of $R^2$ and a lower value of AIC (Table 4), supporting the involvement of DHA in the formation of insoluble products.

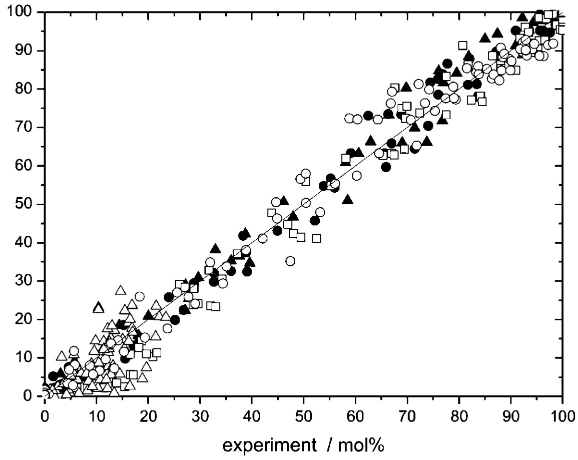


**Figure 10.** Parity plot for experimental data and model predictions (stage 1: □: conversion of DHA, △: yield of PRV, ○: yield of LA; stage 2: ▲: conversion of PRV, ●: yield of LA).

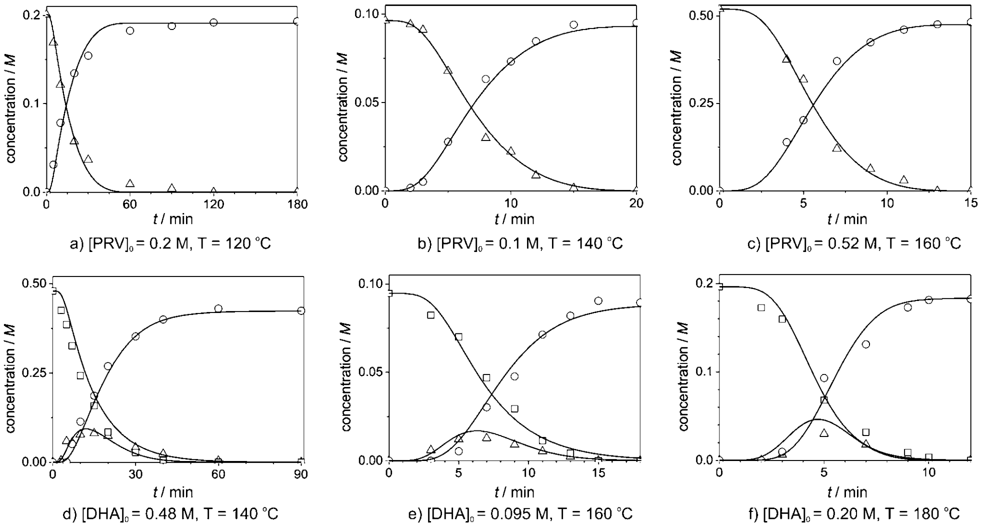
**Table 4.** Model comparison for the conversion of DHA.

| Main reaction ($R_{A1}$) | Side reaction ($R_{A2}$) | $R^2$ | AIC |
|---|---|---|---|
| included | excluded | 0.975 | −906 |
| included | included | 0.982 | −982 |

## Model implications

Experimentally, it was observed that the conversion of DHA was not a function of the initial concentration of DHA (see Figure 7 for details), rationalised by assuming that the reaction was first order in DHA. This was also confirmed by the kinetic modelling activities and the order of the reaction for DHA ($\alpha$ in Table 3) was found to be close to one.

The exploratory studies also revealed that the yield of LA was a function of the initial DHA concentration, with a low initial concentration of DHA leading to higher LA yields (Figure 6b). This may be rationalised by comparing the order of the undesired reactions that form insoluble byproducts ($R_{A2}$ and $R_{B2}$) with that of the desired reactions. The order of the side reactions and, particularly for $R_{B2}$, is far higher (1.30) than the order of the



a) $[PRV]_0$ = 0.2 M, T = 120 °C
b) $[PRV]_0$ = 0.1 M, T = 140 °C
c) $[PRV]_0$ = 0.52 M, T = 160 °C
d) $[DHA]_0$ = 0.48 M, T = 140 °C
e) $[DHA]_0$ = 0.095 M, T = 160 °C
f) $[DHA]_0$ = 0.20 M, T = 180 °C

**Figure 9.** Comparison between experimental data (□: DHA, △: PRV, ○: LA) and the model (——).

others (Table 3). This indicates that the side reaction to give insoluble products may be suppressed by working at lower concentration levels, in agreement with experimental findings.

Figure 11 shows the modelled LA yield as a function of the initial DHA concentration and temperature. It is evident that a high yield of LA is attainable at low initial DHA concentrations and high temperatures, in agreement with the experimental findings.

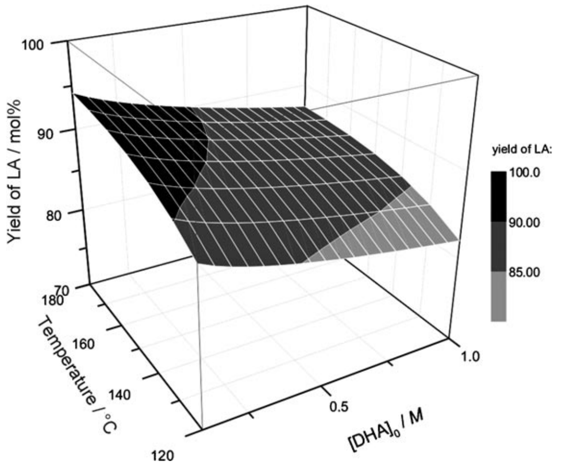


**Figure 11.** Effect of [DHA]$_0$ and temperature on the yield of LA ([AlCl$_3$] = 10 mM, 100% conversion of DHA).

## Conclusions

The potential of metal salts as catalysts for the conversion of the trioses DHA and GLY into LA in aqueous solutions has been explored. $Al^{3+}$ and $Cr^{3+}$ were found to be the most promising cations and LA yields of up to 93 mol% were obtained. A reaction pathway was proposed that involved PRV as the intermediate. A kinetic model was developed for the conversion of DHA to LA by using Al salts. The model implies that high LA yields were attainable by performing the reaction at low initial concentrations of DHA at the highest temperature in the range studied (180 °C).

The findings of this study are also relevant for the development of improved heterogeneous catalysts for the conversion of DHA into LA in aqueous solutions. Based on this study, solid catalysts with Lewis acidic $Al^{3+}$ or $Cr^{3+}$ sites may be very promising. In addition, our study also shows that homogeneous systems are useful model systems for heterogeneous counterparts to gain insights into mechanistic pathways.

The conversion of trioses to LA may be envisaged as an alternative for the currently applied fermentation route to LA, providing that the trioses are readily available. Potential sources for the trioses are cheap hexoses, such as D-glucose,[7a,b,g] pyrolysis oil fractions which may contain up to 4 wt% of DHA and PRV[11] or glycerol,[12] which is a main byproduct of biodiesel processes.

## Experimental Section

Materials and methods: DHA dimer (97%), GLY (≥98%), PRV (40 wt%) and standardised 1 mol L$^{-1}$ LA were purchased from Sigma Aldrich (Schnelldorf, German). The halide and sulfate salts were purchased from Merck KGaA (Darmstadt, Germany), apart from $AlCl_3{\cdot}6\,H_2O$, $CrCl_3{\cdot}6\,H_2O$ and $Fe_2(SO_4)_3{\cdot}x\,H_2O$, which were purchased from Sigma Aldrich (Schnelldorf, German), and anhydrous $CrCl_2$ and $LaCl_3$, which were obtained from Acros Organics (Geel, Belgium).

The reactions were carried out in glass ampoules with an inside diameter of 3 mm, wall thickness of 1.5 mm and length of 150 mm. The glass ampoules containing a predetermined amount of salt in aqueous solution of triose were sealed by using a torch and placed in a constant oven temperature. Typical experiments were conducted according to experimental procedures described in a previous study.[7g]

The amounts of DHA, GLY, PRV and LA were quantified by using a HPLC instrument with an RI detector and a Biorad Aminex HPX-87H column. A capillary electrophoresis (CE) system from Agilent Technologies was used to determine the amount of LA in the aqueous phases. Detailed descriptions of the HPLC and CE methods are described elsewhere.[7g]

An Inolab pH 730 instrument equipped with a Sentix 81 probe was used to measure the pH of the reaction mixtures at room temperature.

## Acknowledgements

*C.B.R. thanks the University of Groningen for financial support to perform his Ph.D. study with a Bernoulli Scholarship.*

**Keywords:** kinetics · lactic acid · renewable resources · sustainable chemistry · trioses

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Received: December 29, 2010