

Electronic Supplementary Material for :

Dihydroxyacetone conversion into lactic acid in aqueous media in the presence of metal salts: influence of the ionic thermodynamic equilibrium on the reaction performance

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Reaction mechanism

In order to identify the reaction mechanism leading to the formation of the brown soluble oligomers, a complete model – i.e. taking into account all the oligomerization reactions proposed in the literature - was implemented. The global reaction mechanism corresponding to the model is presented on Figure 1.

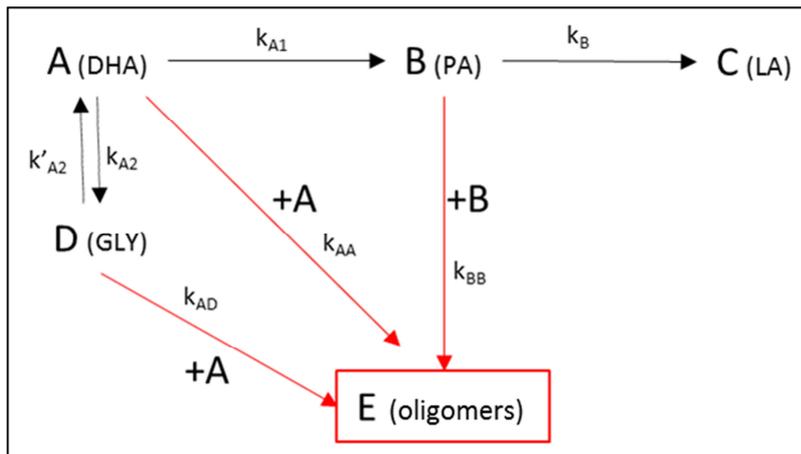


Figure 1: reaction mechanism supposing 3 different paths for formation of oligomers.

The equations of the model corresponding to the mechanism proposed on Figure 1 are :

$$\frac{dA}{dt} = -k_{A1} \cdot A - k_{A2} \cdot A + k'_{A2} \cdot D - k_{AD} \cdot AD - k_{AA} \cdot A^2 \quad (1)$$

$$\frac{dB}{dt} = k_{A1} \cdot A - k_{BB} \cdot B^2 - k_{B1} \cdot B \quad (2)$$

$$\frac{dC}{dt} = k_{B1} \cdot B \quad (3)$$

$$\frac{dD}{dt} = k_{A2} \cdot A - k'_{A2} \cdot D - k_{AD} \cdot AD \quad (4)$$

$$\frac{dE}{dt} = k_{AD} \cdot AD + k_{BB} \cdot B^2 + k_{AA} \cdot A^2 \quad (5)$$

where A, B, C, D et E are the different species concentrations in mol/L (M).

The model contains 7 unknown variables (the kinetic constants of the 7 reactions envisaged), k_{A2} and k'_{A2} being linked through the reaction equilibrium constant K_{AD} :

$$K_{AD} = \frac{k_{A2}}{k'_{A2}} \quad (6)$$

Equations (1) to (5) were numerically solved with the SCILAB software using the ode function. Function optim was used for the parameters estimation, the objective function being the least square difference between the experimental and simulated concentrations.

So as to evaluate the predominant oligomer formation mechanism, the 7 kinetic parameters were estimated for two experiments conducted with $ZnSO_4$ and $ErCl_3$, because these two salts produce a huge quantity of oligomers, and should therefore enable a more precise estimation of the oligomerization kinetic parameters. The experimental conditions and the resulting estimated kinetic parameters are detailed on Table 1.

| Experimental conditions | | |
|--|-----------------------------|-----------------------------|
| Salt | ZnSO ₄ | ErCl ₃ |
| Salt concentration (M) | 0.094 | 0.084 |
| Temperature (°C) | 92 | 87 |
| Initial DHA concentration (M) | 0.094 | 0.085 |
| Estimated kinetic parameters (no constraints) | | |
| k_{A1} (s ⁻¹) | 1.38 10 ⁻⁵ | 2.04 10 ⁻⁵ |
| k_{A2} (s ⁻¹) | 5.25 10 ⁻⁵ | 5.32 10 ⁻⁵ |
| k_{B1} (s ⁻¹) | 2.70 10 ⁻⁵ | 3.27 10 ⁻⁵ |
| k_{AD} (M ⁻¹ s ⁻¹) | 5.21 10⁻³ | 1.91 10⁻³ |
| k_{AA} (M ⁻¹ s ⁻¹) | 0 | 0 |
| k_{BB} (M ⁻¹ s ⁻¹) | 9.48 10⁻⁵ | 0 |
| K_{AD} (-) | 0.14 | 0.11 |
| Objective function ϵ (-) | 1.3 10 ⁻⁵ | 2.04 10 ⁻⁵ |
| Estimated kinetic parameters ($k_{AD} = 0$) | | |
| k_{A1} (s ⁻¹) | 2.35 10 ⁻⁵ | 2.35 10 ⁻⁵ |
| k_{A2} (s ⁻¹) | 1.69 10 ⁻⁵ | 2.22 10 ⁻⁵ |
| k_{B1} (s ⁻¹) | 3.93 10 ⁻⁵ | 3.88 10 ⁻⁵ |
| k_{AD} (M ⁻¹ s ⁻¹) | 0 | 0 |
| k_{AA} (M ⁻¹ s ⁻¹) | 3.44 10⁻⁴ | 0.01 |
| k_{BB} (M ⁻¹ s ⁻¹) | 1.28 10⁻³ | 0 |
| K_{AD} (-) | 0.21 | 0.13 |
| Objective function ϵ (-) | 5 10 ⁻⁴ | 9.1 10 ⁻⁵ |

Table 1: experimental conditions and estimated kinetic parameters

The estimation procedure was carried out in two steps.

First, no constraints were applied to the parameters values, i.e. no lower or upper bound was applied. As can be seen in Figure 2, the resulting simulated concentration curves fit very well the experimental point for all species and for both salts, which validates the postulated reaction mechanism schematized in Figure 1. Moreover (see Table 1), the estimated kinetic parameters for

the three oligomerization reactions vary by several order of magnitude: k_{AD} is 50 times greater than k_{BB} and k_{AA} converges to 0. This indicates that the aldol condensation of DHA with GLY is the predominant path to the formation of oligomers.

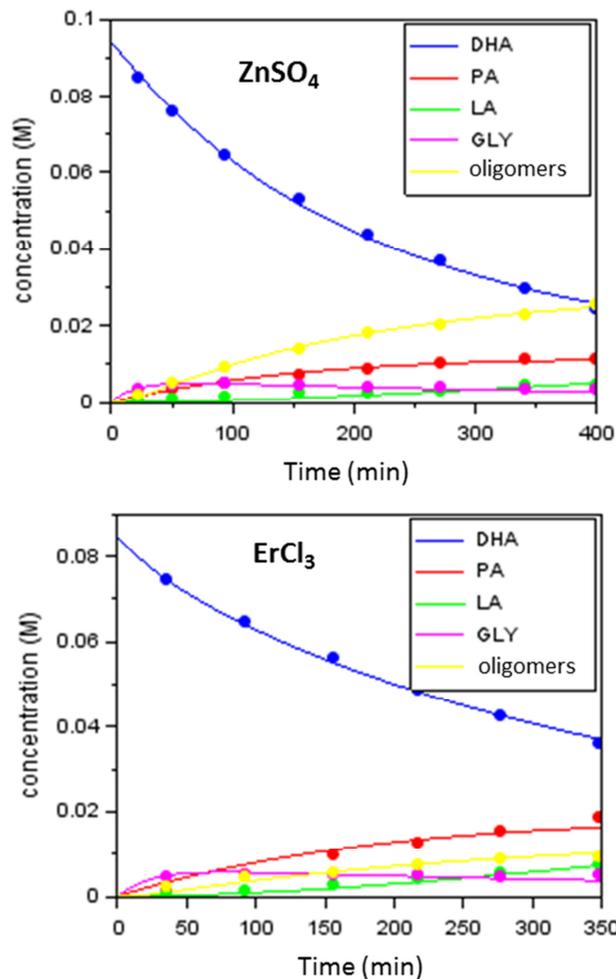


Figure 2: simulated and experimental concentration curves when all the oligomerization mechanism are taken into account

In order to reinforce this conclusion, a second parameter estimation was performed, supposing that $k_{AD} = 0$ (no aldol condensation of DHA with GLY). The objective is to test the model sensivity to the different oligomerization pathways, so as to conclude on the possibility to differenciate the different oligomerization mechanisms. As can be seen in Figure 3, the model cannot fit the experimental data as accurately when the aldol condensation of DHA with GLY is neglected. The objective functions ϵ are indeed much higher for the two salts.

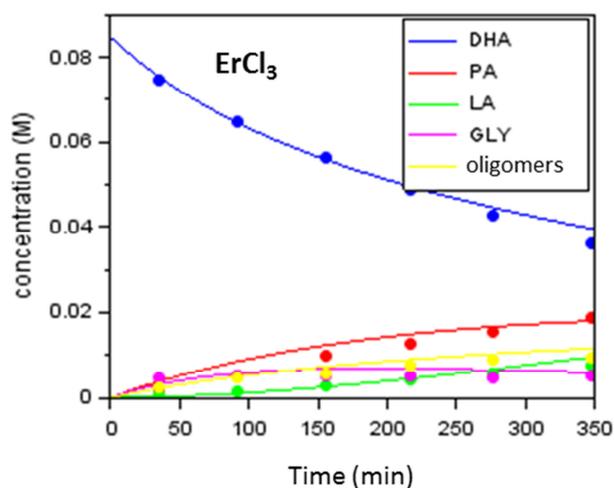
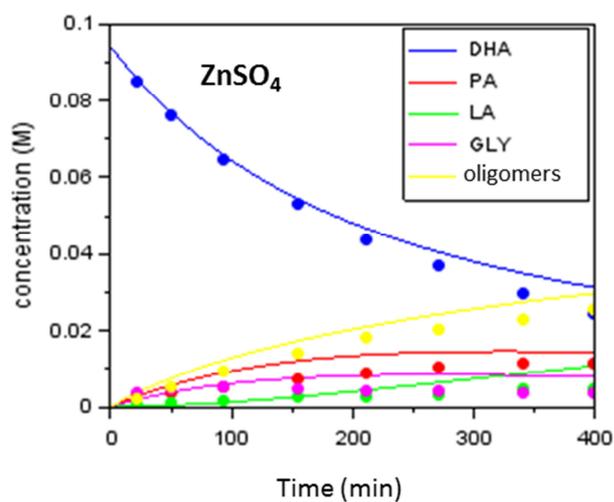


Figure 3: simulated and experimental concentration curves when the aldol condensation of DHA with GLY is neglected

As a conclusion, DHA+DHA or PA+PA oligomerization cannot quantitatively explain the oligomer formation in our experimental conditions. These two reactions were therefore neglected in the rest of this study.

Activation energies

The reactions activation energies were evaluated for sulfuric acid and aluminium sulphate in the experimental conditions detailed in Table 2.

| Experimental conditions | |
|-------------------------|--------------------------|
| Salts conc. (M) | 0.09 ± 0.005 |
| Temperature (°C) | 70 to 93 |
| DHA initial conc. (M) | 0.09 ± 0.005 |
| Activation energies | |
| catalyst | H_2SO_4 $Al_2(SO_4)_3$ |

| | | |
|----------------------|----|------------|
| Reaction A1 (DHA→PA) | 92 | 98 (93.5*) |
| Reaction B (PA→LA) | | 82 (91.8*) |

Table 2 : experimental conditions and estimated activation energies (*Lux and M. Siebenhofer, *Chem. Biochem. Eng. Q.*, 2016, **29**(4), 575)

The influence of temperature on the different kinetic parameters are depicted on Figure 4 for $\text{Al}_2(\text{SO}_4)_3$ and on Figure 5 for H_2SO_4 . The activation energies for reaction A2 (isomerization of DHA into GLY) and reaction AB (i.e. oligomerization) cannot be evaluated for these catalysts because the concentration in GLY and in oligomers are very low during the whole course of the reaction.

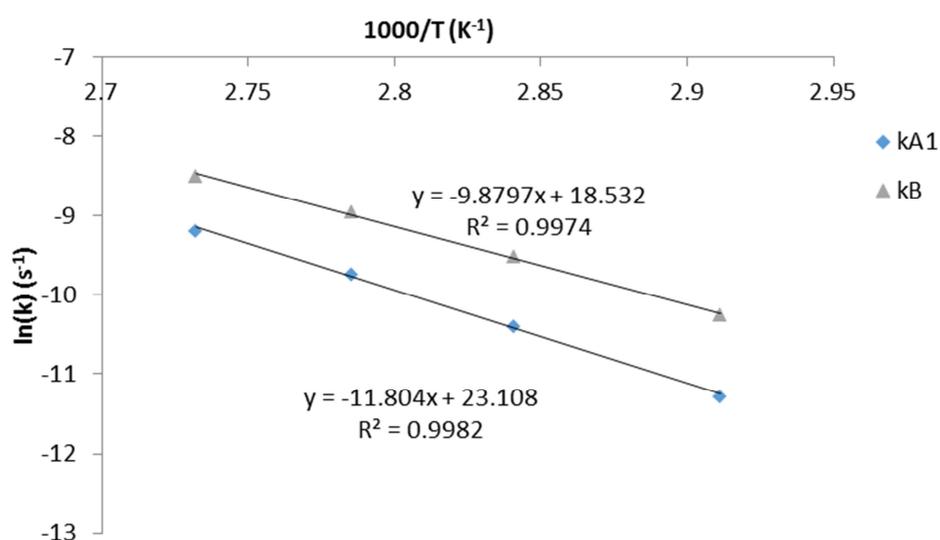


Figure 4 : evolution of the kinetic constants with temperature for $\text{Al}_2(\text{SO}_4)_3$

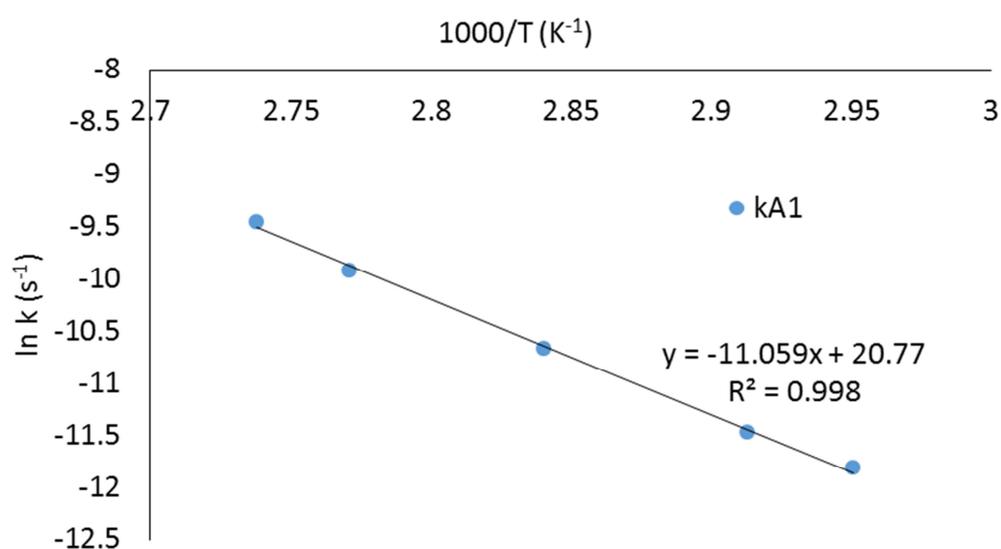


Figure 5 : evolution of the kinetic constants with temperature for H_2SO_4

As can be seen in Table 2, the activation energies for reaction A1 are very close for both catalysts.

As expected from the high yield in LA obtained with aluminium sulphate, the activation energy for reaction B is smaller than that of reaction A1. The values are also coherent with that obtained by Lux et al., taking into account that the experiments were performed at different catalyst concentrations (0.09 M vs. 0.56 M), that is to say with different active aluminium species in the reaction media.