Electronic Supplementary Material (ESI) for Reaction Chemistry & Engineering.

Supporting Information for

Influence of pH on the Kinetics of Hydrolysis Reactions: The Case of Epichlorohydrin and Glycidol

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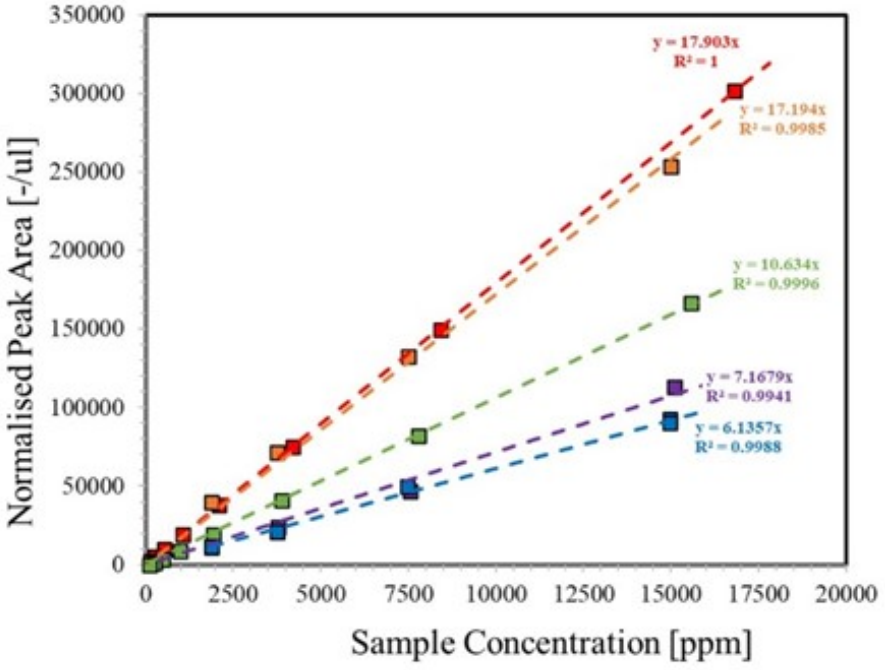

Figure S1. *HPLC external calibration curve for:*

■ *GLY;* ■ *GL;* ■ *MCPD;* ■ *DCP;* ■ *EPI.*

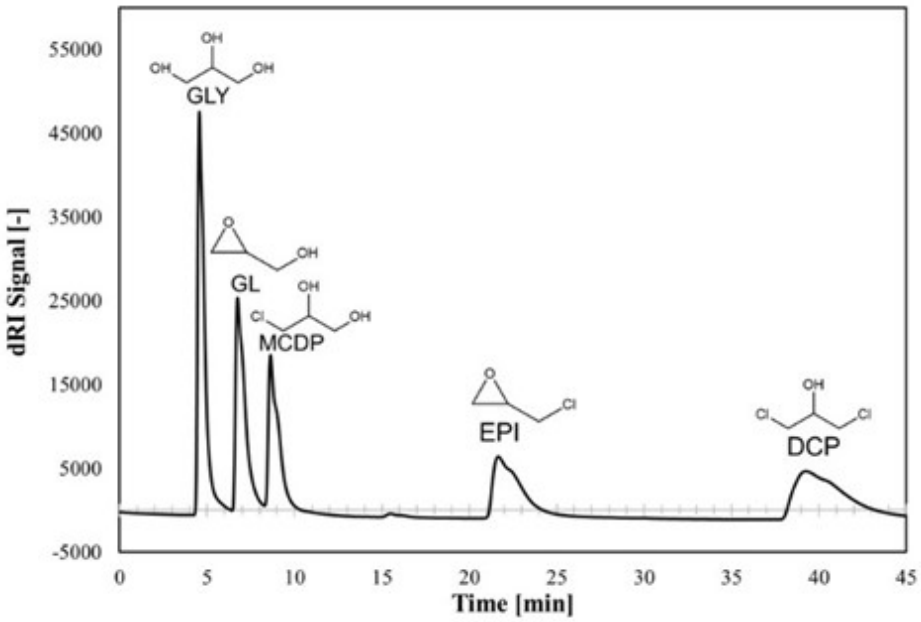

Figure S2. *Example of HPLC elugram used to characterize the reaction mixture.*

Table S1. *Residence time and external calibration for the HPLC method.*

species	*rt [min]*	*m*	r^2
GLY	4.54	17.903	0.9992
GL	6.84	10.634	0.9996
MCPD	8.767	17.194	0.9985
EPI	15.94	6.1357	0.9988
DCP	22.48	7.1679	0.9941

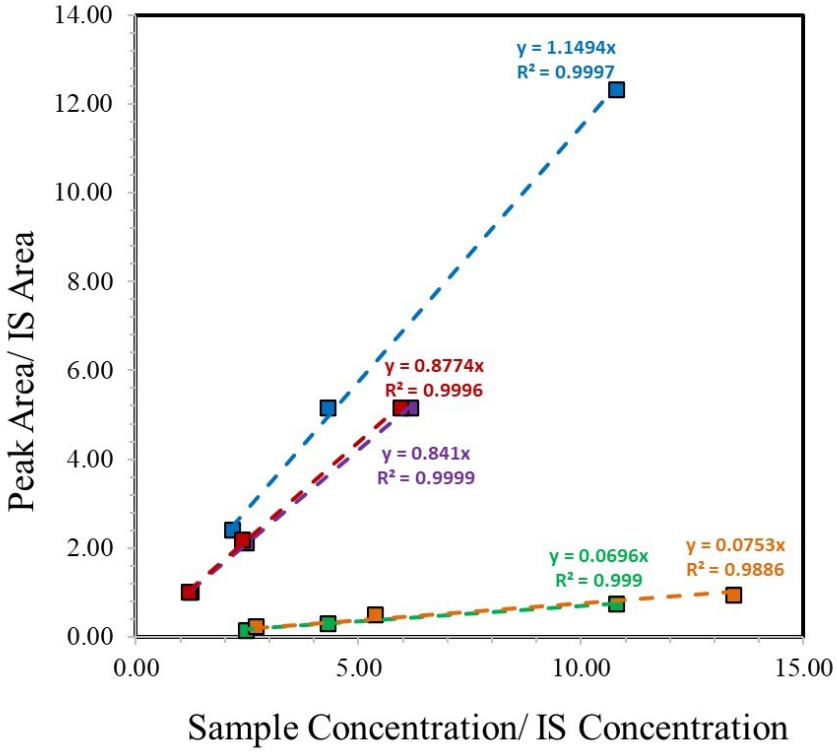

Figure S3. *GC internal calibration curve.* ■ *GL;* ■ *MCPD;* ■ *1,3-DCP;* ■ *1,2-DCP;* ■ *EPI.*

Table S2. *Residence time and internal calibration for the GC method.*

species	*rt [min]*	*m*	R^2
GL	5.24	0.0696	0.9999
MCPD	9.35	0.0753	0.9886
EPI	3.52	1.1494	0.9997
1,3-DCP	6.58	0.8410	0.9999
1,2-DCP	6.98	0.8774	0.9996

Table S3. *Experimental initial Conditions.*

Exp.	T [°C]	$[EPI]^0$ [mol L^{-1}]	$[Cl]^0$ [mol L^{-1}]	$[MCPD]^0$ [mol L^{-1}]	$[DCP]^0$ [mol L^{-1}]	$[GL]^0$ [mol L^{-1}]	$[GLY]^0$ [mol L^{-1}]	pH^0 [-]
1	20	0.0	0.63	0.00	0.0	0.13	0.0	1.00
2	20	0.0	0.00	0.07	0.0	0.00	0.0	13.25
3	20	0.0	0.10	0.00	0.0	0.13	0.0	1.00
4	20	0.0	0.00	0.00	0.0	0.14	0.0	5.80
5	20	0.0	1.14	0.00	0.0	0.14	0.0	6.50
6	20	0.0	0.00	0.00	0.0	0.14	0.0	13.23
7	30	0.0	0.63	0.00	0.0	0.13	0.0	0.93
8	30	0.0	0.10	0.00	0.0	0.13	0.0	1.00
9	30	0.0	0.00	0.00	0.0	0.14	0.0	13.00
10	40	0.0	0.63	0.00	0.0	0.13	0.0	1.00
11	40	0.0	0.00	0.09	0.0	0.00	0.0	12.70
12	40	0.0	0.10	0.00	0.0	0.13	0.0	0.97
13	40	0.0	0.00	0.00	0.0	0.14	0.0	6.00
14	40	0.0	1.14	0.00	0.0	0.14	0.0	5.70
15	40	0.0	0.00	0.00	0.0	0.14	0.0	12.60
16	50	0.0	0.00	0.00	0.0	0.15	0.0	6.30
17	50	0.0	0.57	0.00	0.0	0.14	0.0	5.80
18	50	0.0	0.00	0.00	0.0	0.14	0.0	12.34
19	60	0.0	0.63	0.00	0.0	0.13	0.0	1.00
20	60	0.0	0.00	0.09	0.0	0.00	0.0	12.20
21	60	0.0	0.10	0.00	0.0	0.13	0.0	1.00
22	60	0.0	0.00	0.00	0.0	0.14	0.0	6.80
23	60	0.0	0.57	0.00	0.0	0.14	0.0	5.60
24	60	0.0	0.00	0.00	0.0	0.14	0.0	12.1

Table S3. *Experimental initial Conditions.*

Exp.	T [°C]	$[EPI]^0$ [mol L^{-1}]	$[Cl]^0$ [mol L^{-1}]	$[MCPD]^0$ [mol L^{-1}]	$[DCP]^0$ [mol L^{-1}]	$[GL]^0$ [mol L^{-1}]	$[GLY]^0$ [mol L^{-1}]	pH^0 [-]
25	20	0.10	1.16	0.00	0.00	0.00	0.00	1.00
26	20	0.00	0.00	0.00	0.10	0.00	0.00	13.40
27	20	0.11	0.10	0.00	0.00	0.00	0.00	0.96
28	20	0.11	0.00	0.00	0.00	0.00	0.00	5.20
29	20	0.11	1.14	0.00	0.00	0.00	0.00	5.70
30	20	0.05	0.00	0.00	0.00	0.00	0.00	13.00
31	30	0.10	0.10	0.00	0.00	0.00	0.00	1.00
32	30	0.11	0.00	0.00	0.00	0.00	0.00	13.00
33	40	0.10	0.63	0.00	0.00	0.00	0.00	0.90
34	40	0.00	0.00	0.00	0.10	0.00	0.00	12.80
35	40	0.10	0.10	0.00	0.00	0.00	0.00	1.10
36	40	0.11	0.00	0.00	0.00	0.00	0.00	6.90
37	40	0.11	1.14	0.00	0.00	0.00	0.00	5.60
38	40	0.11	0.00	0.00	0.00	0.00	0.00	12.80
39	50	0.10	0.63	0.00	0.00	0.00	0.00	1.00
40	50	0.11	0.00	0.00	0.00	0.00	0.00	6.90
41	50	0.10	0.57	0.00	0.00	0.00	0.00	6.20
42	50	0.11	0.00	0.00	0.00	0.00	0.00	12.40
43	60	0.10	1.16	0.00	0.00	0.00	0.00	1.00
44	60	0.00	0.00	0.00	0.08	0.00	0.00	12.10
45	60	0.11	0.10	0.00	0.00	0.00	0.00	1.00
46	60	0.11	0.00	0.00	0.00	0.00	0.00	6.80
47	60	0.11	1.14	0.00	0.00	0.00	0.00	6.80
48	60	0.11	0.00	0.00	0.00	0.00	0.00	11.90

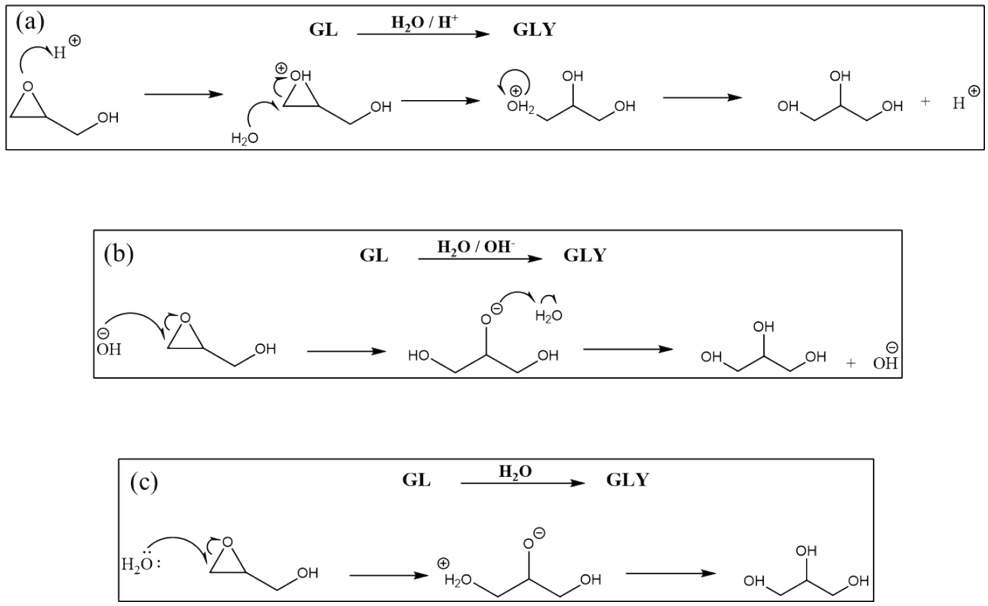

Figure S4 *– Reaction mechanism of GL hydrolysis. (a) Acid conditions. (b) Alkaline conditions. (c) Neutral conditions.*

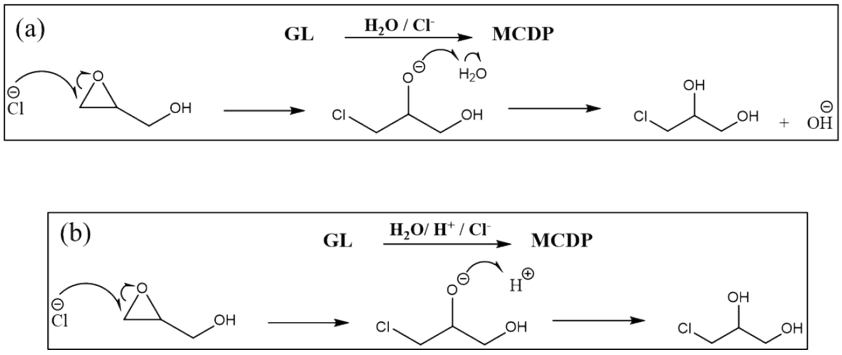

Figure S5 *– Reaction mechanism of GL chlorination. (a) Neutral conditions. (b) Acid conditions.*

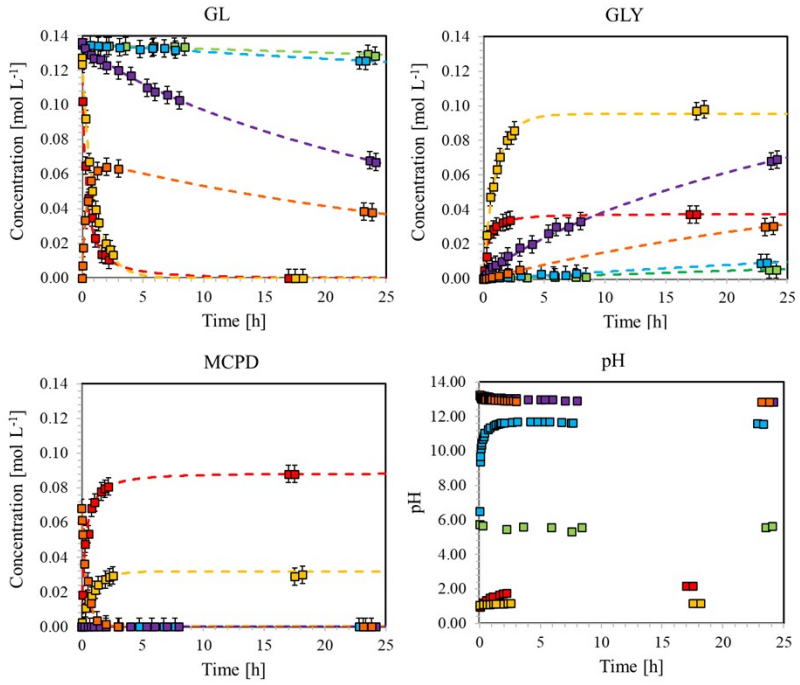

Figure S6 *- GL reactivity at T = 20°C. Dotted line: model prediction. Square: Experimental data. (Red): exp.1, (Orange): exp.2, (Yellow): exp.3, (Green): exp.4, (Light-Blue): exp.5, (Purple): exp.6.*

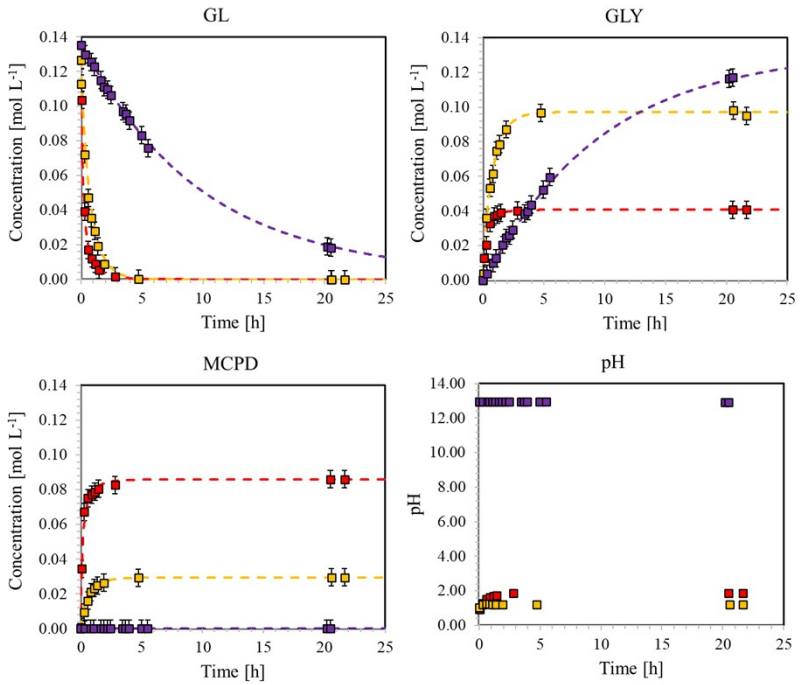

Figure S7 *- GL reactivity at T = 30°C. Dotted line: model prediction. Square: Experimental data. (Red): exp.7, (Yellow): exp.8, (Purple): exp.9.*

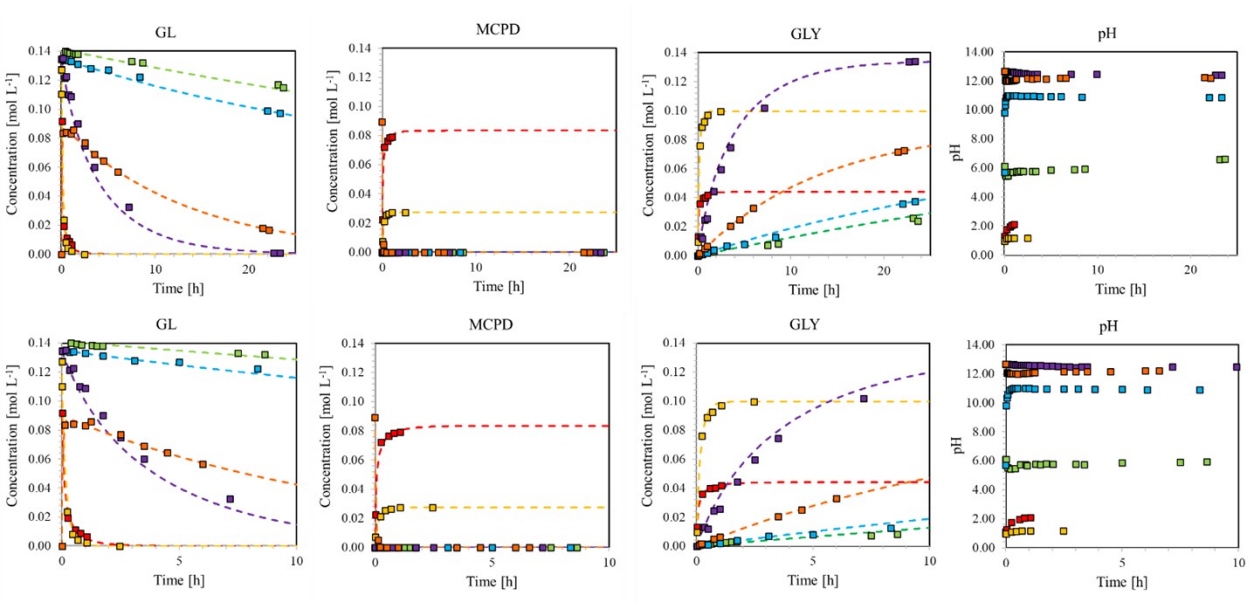

Figure S8 *– Top row: Time evolution of the concentrations of GL, GLY and MCDP as well as of pH during hydrolysis of GL and dehydrohalogenation of MCPD at T = 40 °C. Dotted curves: model predictions. Symbols: Experimental data. (Red): exp.10, (Orange): exp.11, (Yellow): exp.12, (Green): exp.13, (Light-Blue): exp.14, (Purple): exp.15. Experimental conditions as in Table S3. Bottom row: Magnification of the first 10 h of the process for the same experiments.*

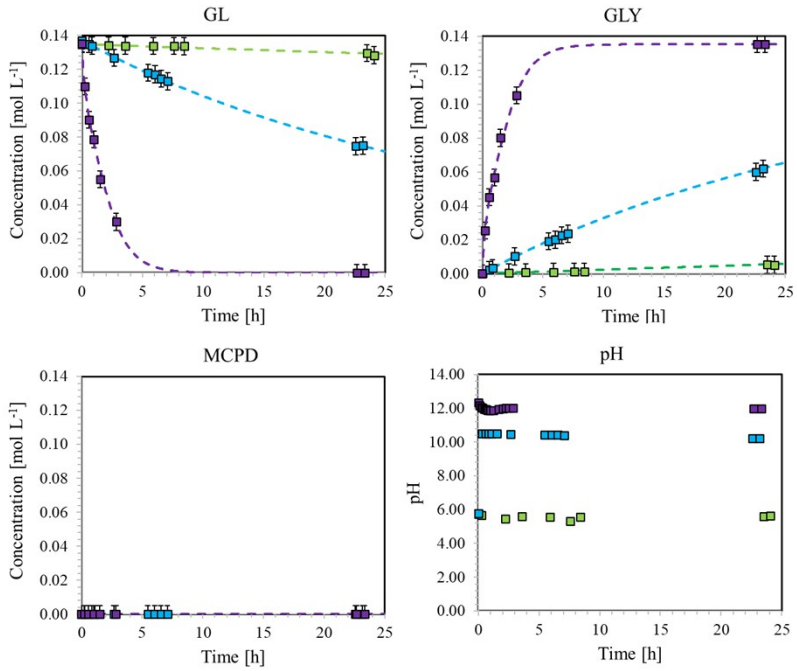

Figure S9 *- GL reactivity at T = 50°C. Dotted line: model prediction. Square: Experimental data. (Green): exp.16, (Light-Blue): exp. 17, (Purple): exp.18.*

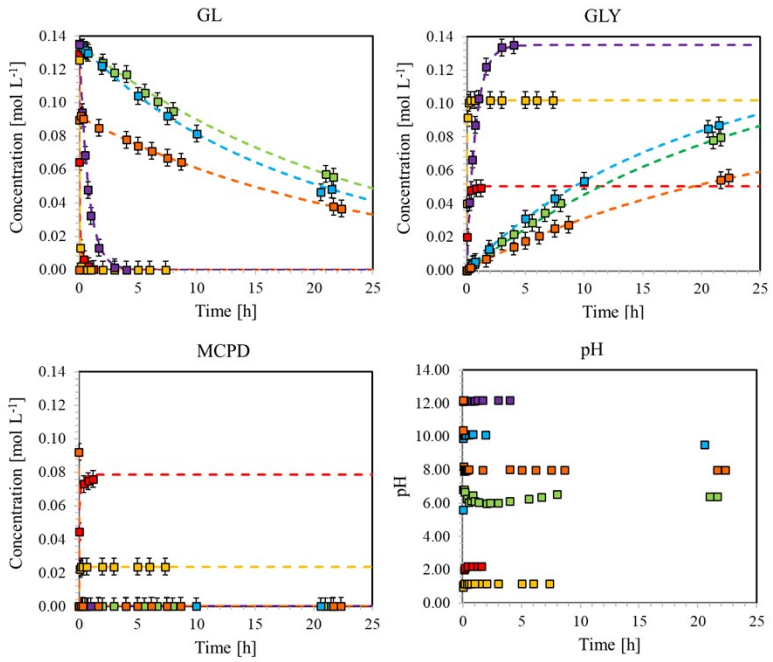

Figure S10 *- GL reactivity at T = 60°C. Dotted line: model prediction. Square: Experimental data. (Red): exp.19, (Orange): exp.20, (Yellow): exp.21, (Green): exp.22, (Light-Blue): exp. 23, (Purple): exp.24.*

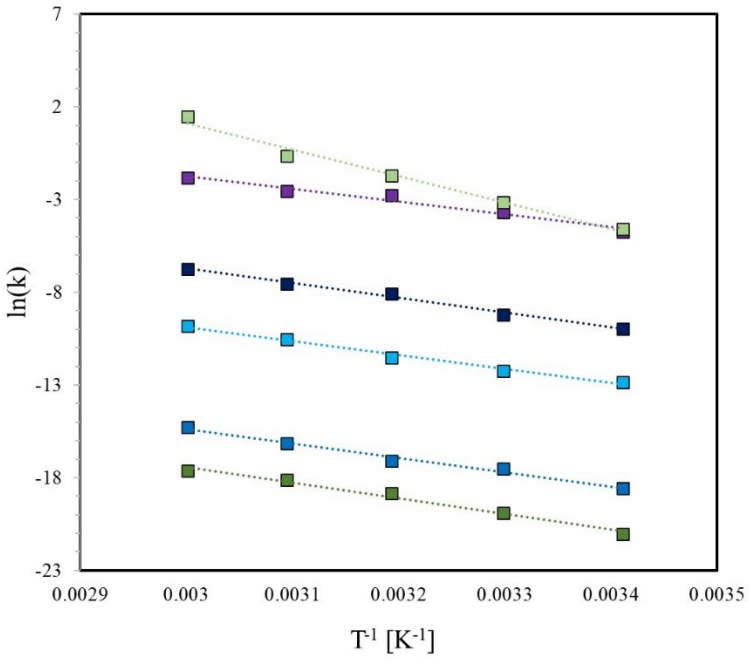

Figure S11 *- Arrhenius plot of the rate constants in Table 1. (■) $k_{h,GL}^{acid}$. (■) $k_{h,GL}^{neutral}$.(■) $k_{h,GL}^{alkaline}$. (■)$k_{Cl,GL}^{acid}$. (■) $k_{Cl,GL}^{neutral}$. (■) $k_{hd,MCPD}^{alkaline}$.*

Table S4 *– Kinetic scheme and reaction rates reported in the literature for the EPI hydrolysis.*

Kinetic Scheme	Reaction rates	Reference
EPI + NaOH + H_2O → GLY + NaCl	R = A exp(-Ea/RT) [EPI][OH^-] A = 9.43 x 10^8 [L mol^{-1} s^{-1}]; Ea = 70790 [J mol^{-1}]; [OH^-] = 0.2 mol L^{-1}	33
EPI + H_2O → MCPD	R = A exp(-Ea/RT) [EPI] A = 4.92 x 10^8 [s^{-1}]; Ea = 78877[J mol^{-1}]; pH = 12	34
EPI + OH^- + H_2O → GLY + Cl^-	R = A exp(-Ea/RT) [EPI] [OH^-] A = 3.42 x 10^{11} [L mol^{-1} s^{-1}]; Ea = 87305[J mol^{-1}]; [OH^-] = 0.2 mol L^{-1}	35

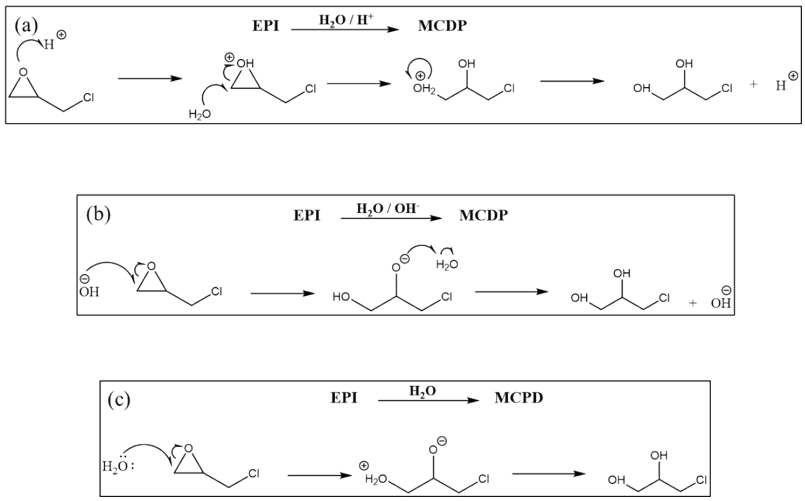

Figure S12 *- Reaction mechanism of EPI hydrolysis. (a) Acid conditions. (b) Alkaline conditions. (c) Neutral conditions.*

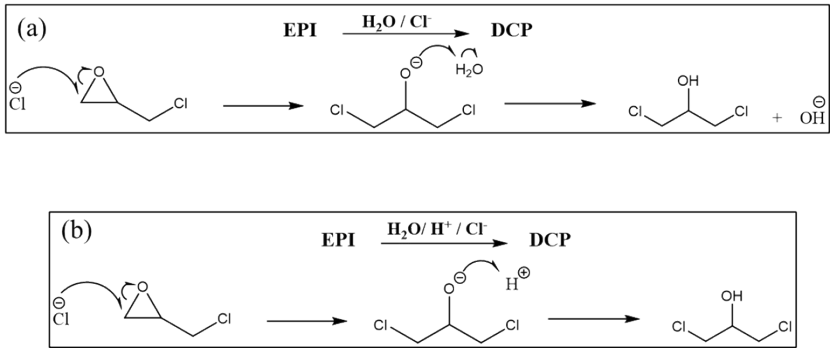

Figure S13 *- Reaction mechanism of EPI chlorination. (a) Neutral conditions. (b) Acid conditions.*

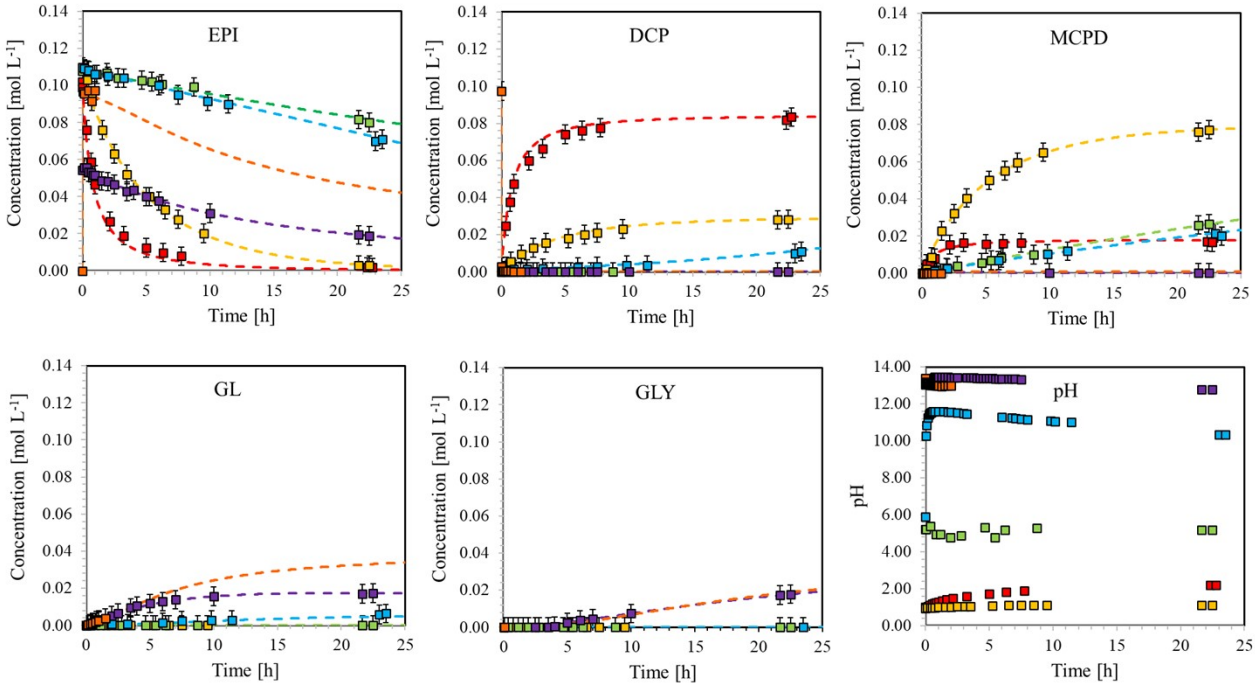

Figure S14 *– EPI reactivity at T = 20°C. Dotted line: model prediction. Square: Experimental data. (Red): exp.25, (Orange): exp.26, (Yellow): exp.27, (Green): exp.28, (Light-Blue): exp.29, (Purple): exp.30.*

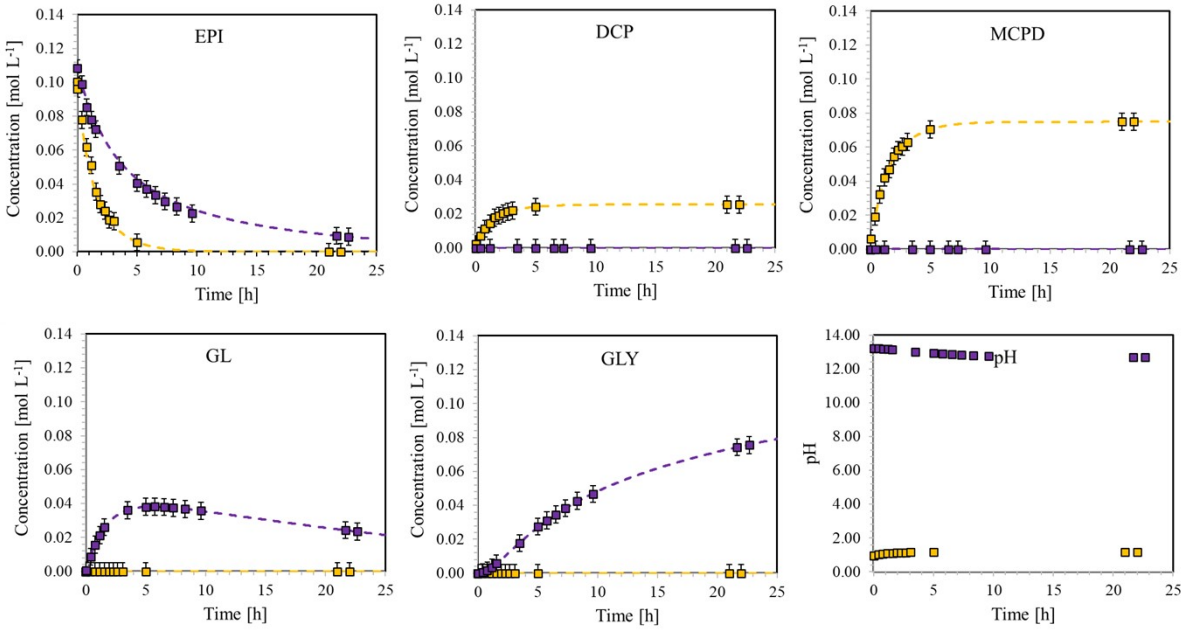

Figure S15 *- EPI reactivity at T = 30°C. Dotted line: model prediction. Square: Experimental data. (Yellow): exp.31, (Purple): exp.32.*

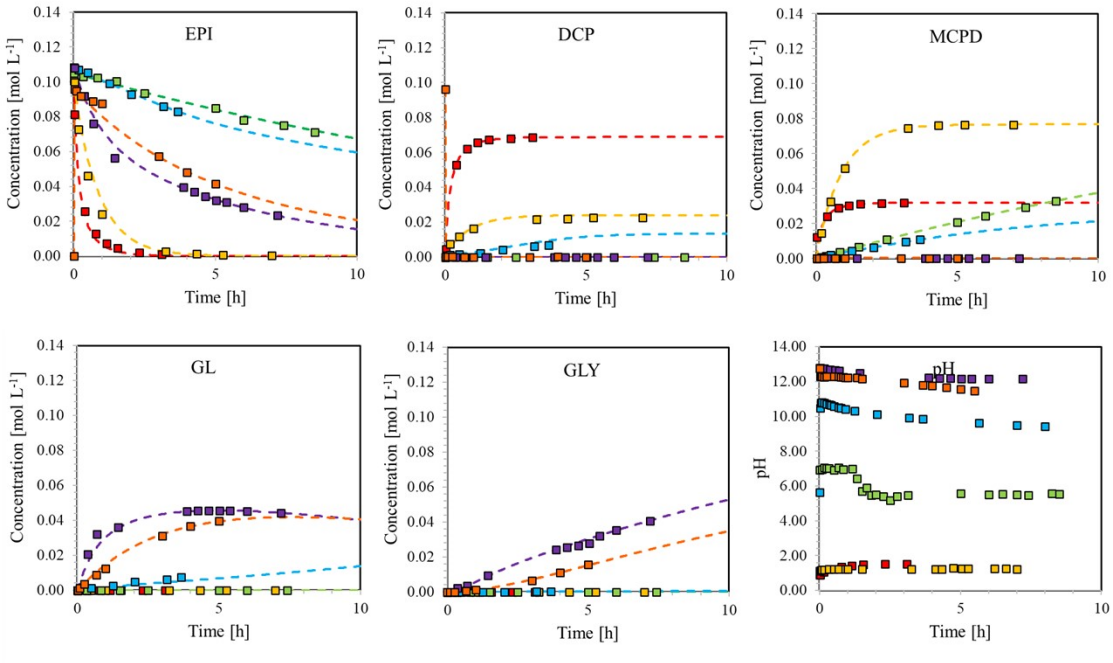

Figure S16– *Concentration of the different species involved in the hydrolysis of EPI and pH values vs. time for the reaction run at T = 40 °C. Dotted curves: model predictions. Squares: Experimental data. (Red): exp.33, (Orange): exp.34, (Yellow): exp.35, (Green): exp.36, (Light-Blue): exp.37, (Purple): exp.38. Experimental conditions as in Table S3.*

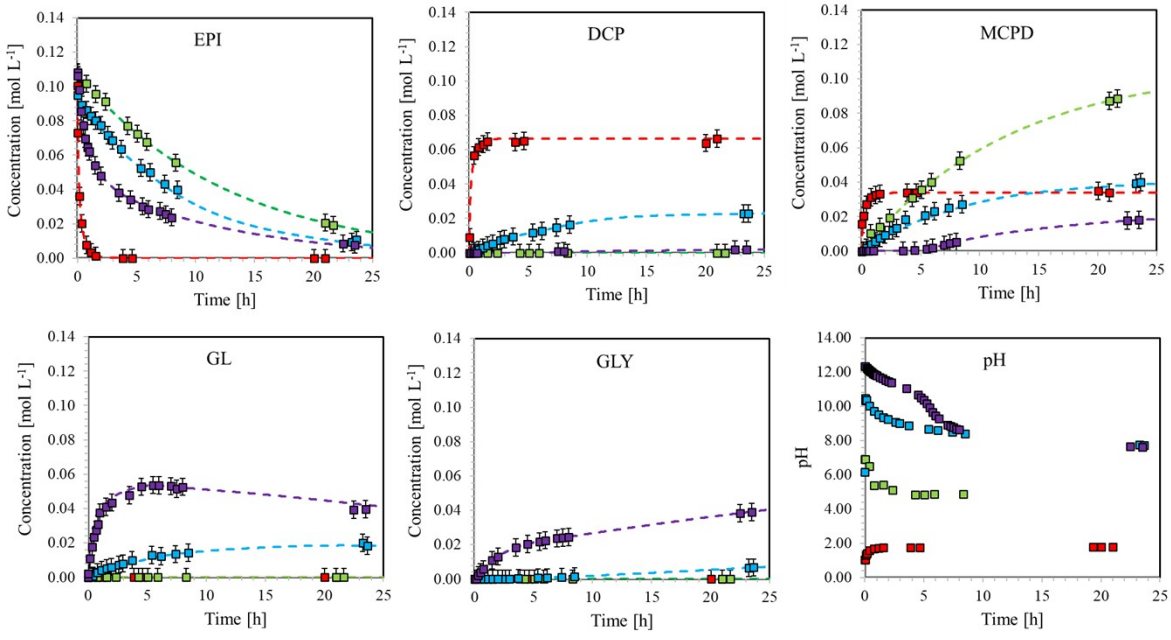

Figure S17 *- EPI reactivity at T = 50°C. Dotted line: model prediction. Square: Experimental data. (Red): exp.39, (Green): exp.40, (Light-Blue): exp.41, (Purple): exp.42.*

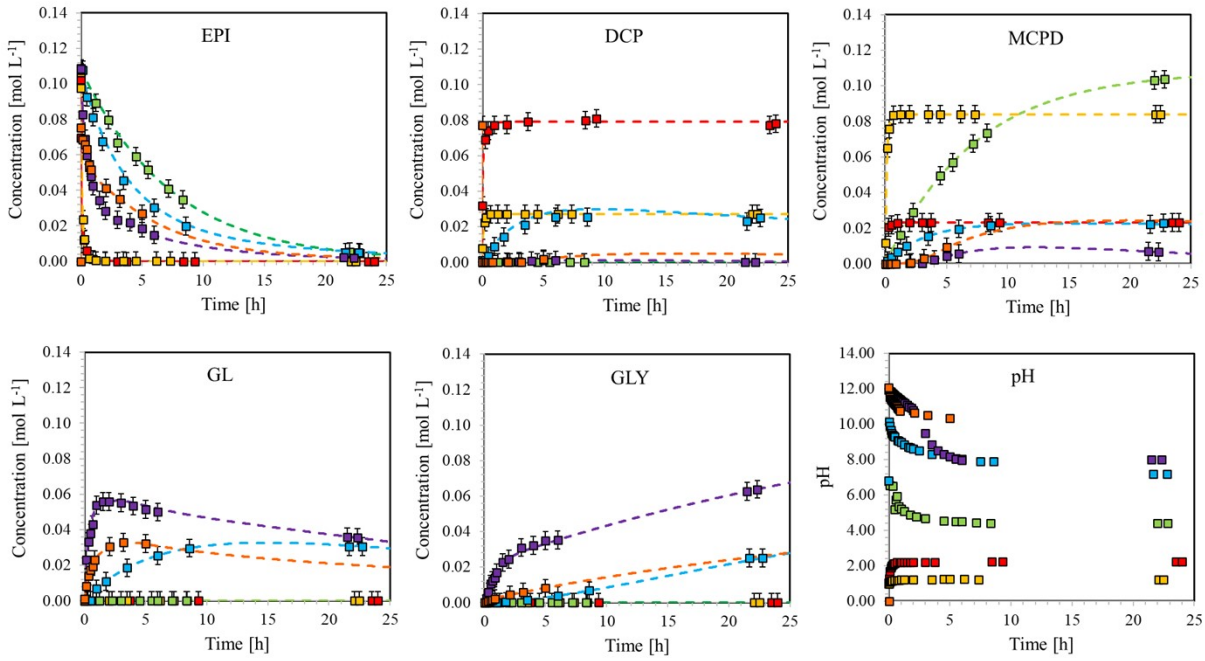

Figure S18– *EPI reactivity at T = 60°C. Dotted line: model prediction. Square: Experimental data. (Red): exp.43, (Orange): exp.44, (Yellow): exp.45, (Green): exp.46, (Light-Blue): exp.47, (Purple): exp.48.*

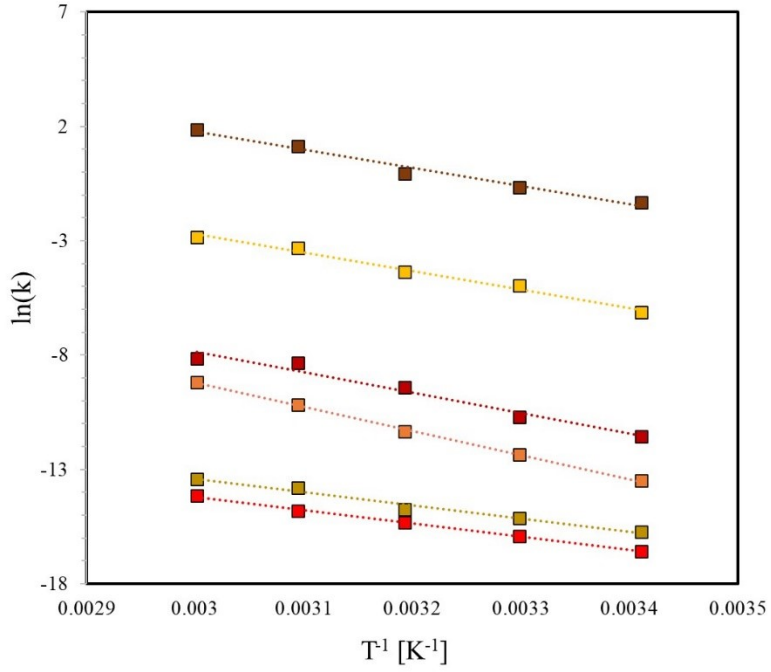

Figure S19 *- Arrhenius plot for the reactions involving EPI. (■) $k_{h,EPI}^{acid}$. (■)$k_{h,EPI}^{neutral}$. (■)$k_{h,EPI}^{alkaline}$. (■) $k_{Cl,EPI}^{acid}$. (■) $k_{Cl,EPI}^{neutral}$. (■) $k_{hd,DCP}^{alkaline}$.*

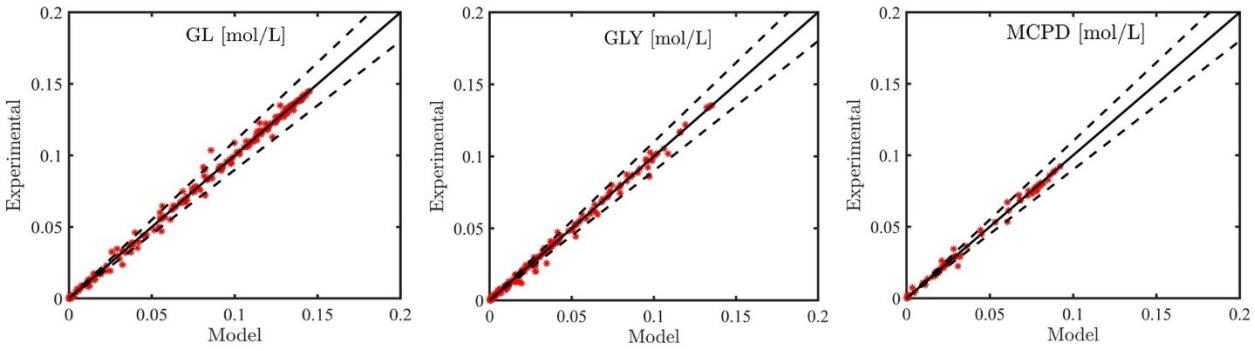

Figure S20*- Parity plot GL reactivity.*

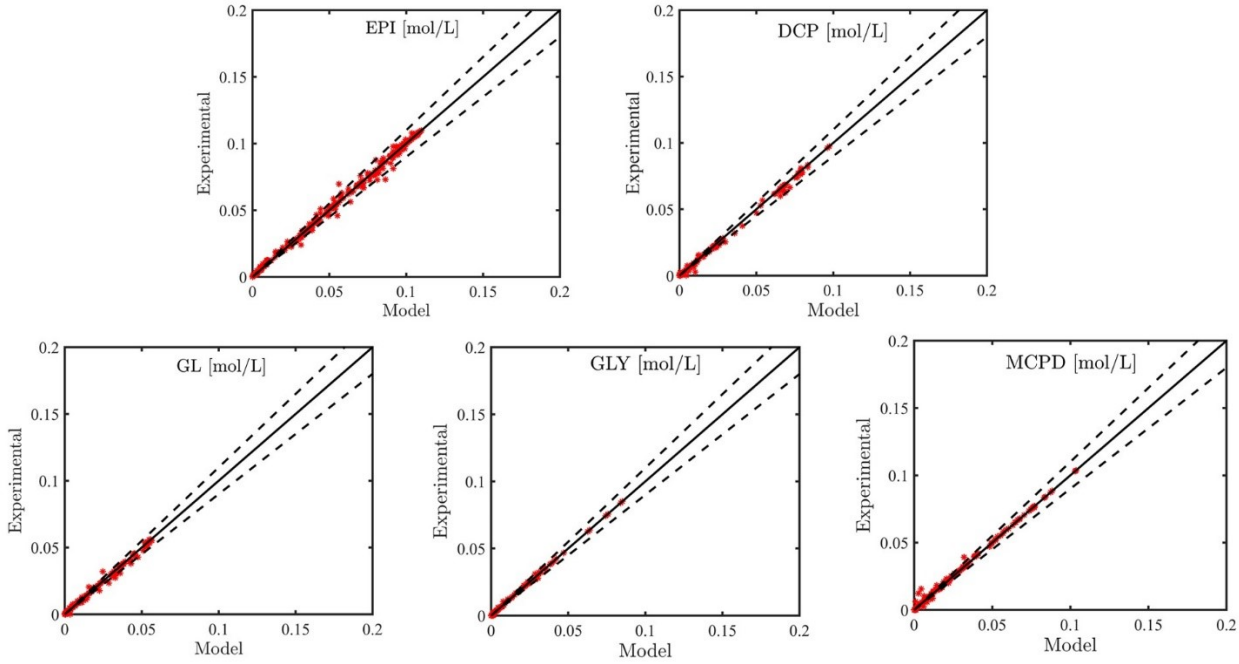

Figure S21*- Parity plot EPI reactivity.*

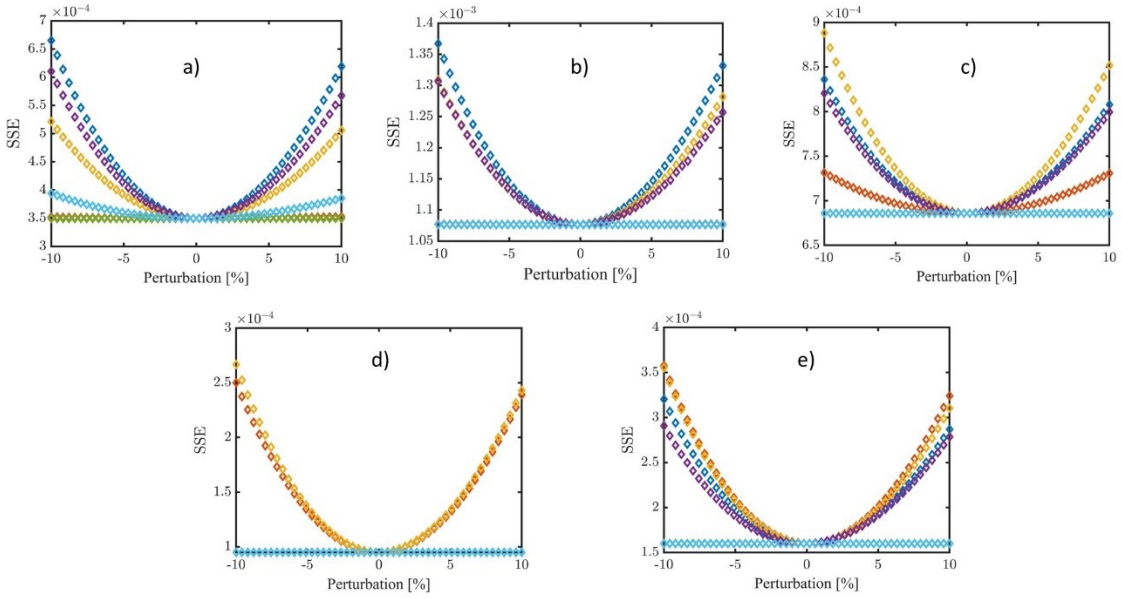

Figure S22 *- Sensitivity analysis. a) 20°C, b) 30°C, c) 40°C, d) 50°C, e) 60°C.* $k_{h,GL}^{acid}$, $k_{h,GL}^{neutral}$, $k_{h,GL}^{alkaline}$, $k_{Cl,GL}^{acid}$, $k_{Cl,GL}^{neutral}$, $k_{hd,MCPD}^{alkaline}$.

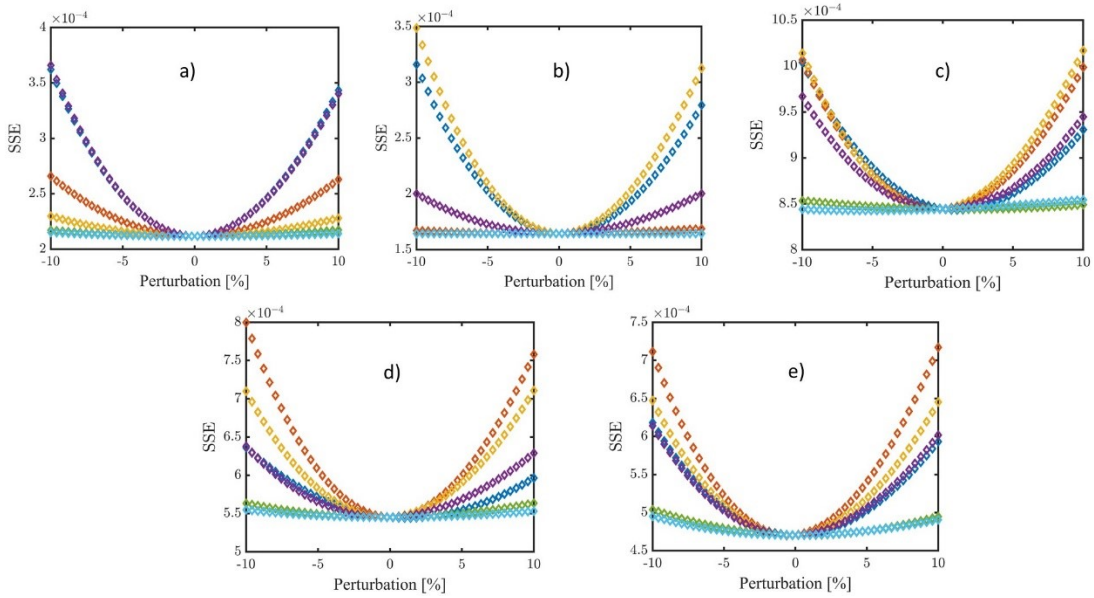

Figure S23 *- Sensitivity analysis. a) 20°C, b) 30°C, c) 40°C, d) 50°C, e) 60°C.* $k_{h,EPI}^{acid}$, $k_{h,EPI}^{neutral}$, $k_{h,EPI}^{alkaline}$, $k_{Cl,EPI}^{acid}$, $k_{Cl,EPI}^{neutral}$, $k_{hd,DCP}^{alkaline}$.