

# Supporting Information

## Kinetic Model for the Dehydration of Xylose to Furfural from a Boronate Diester Precursor

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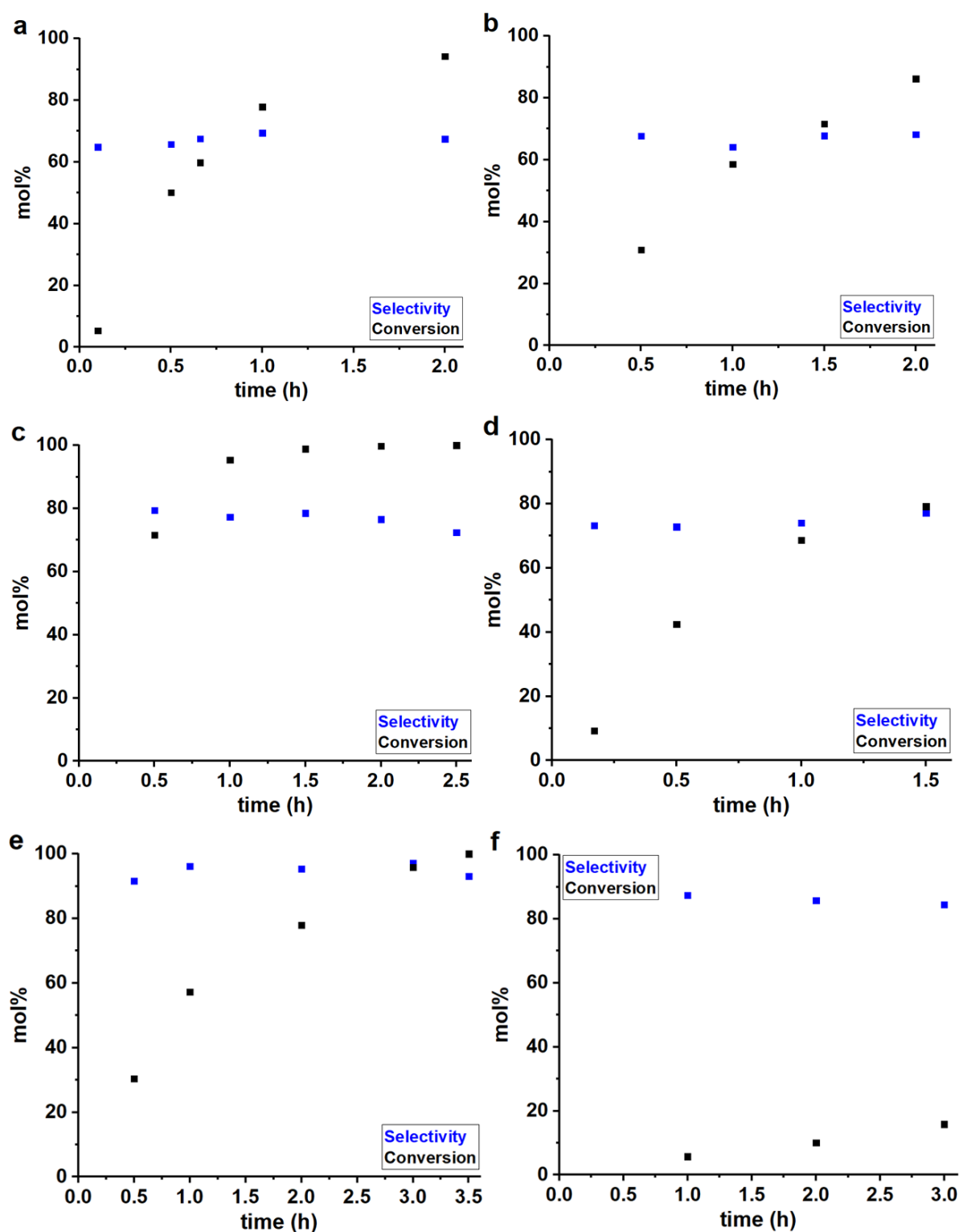
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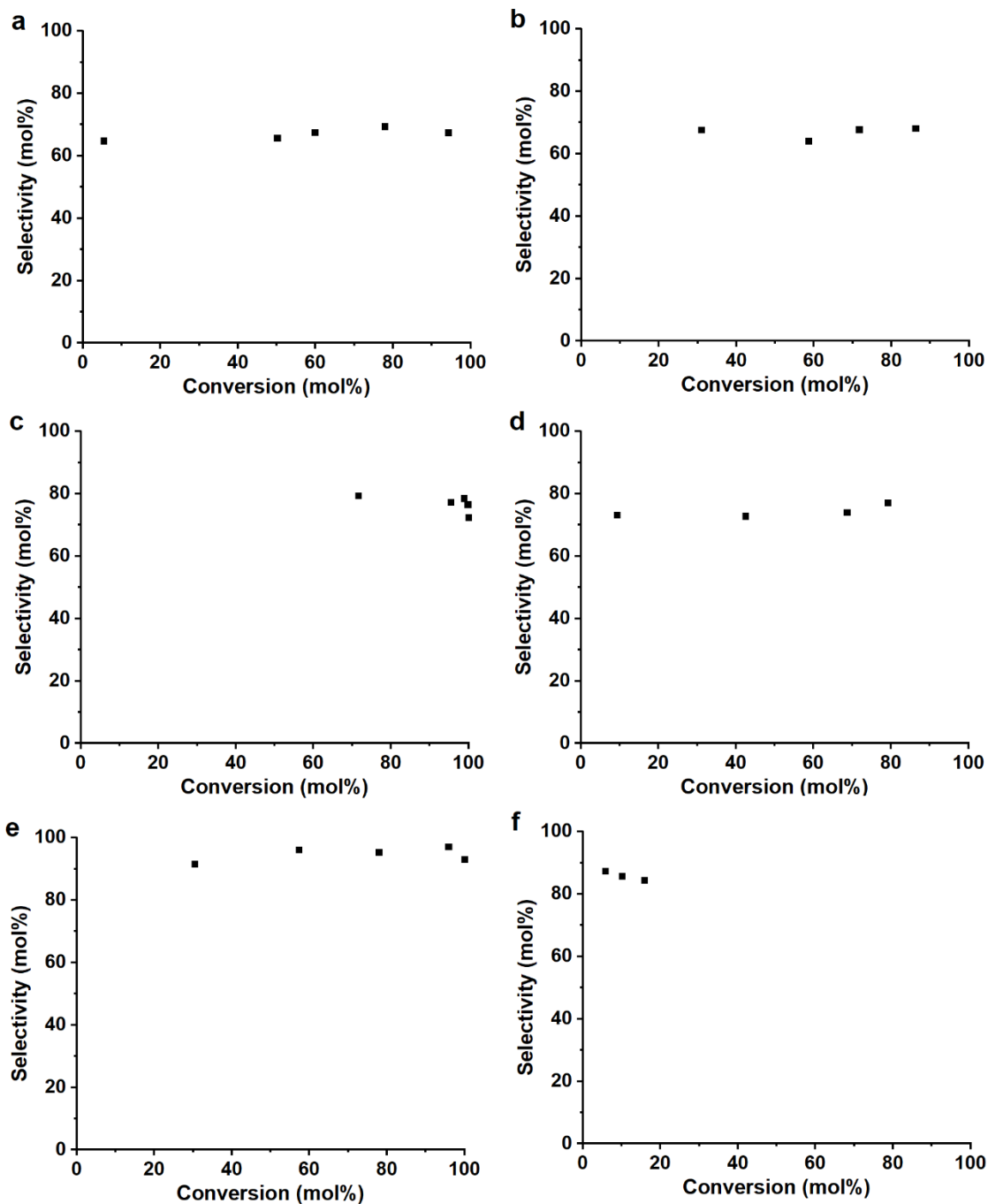
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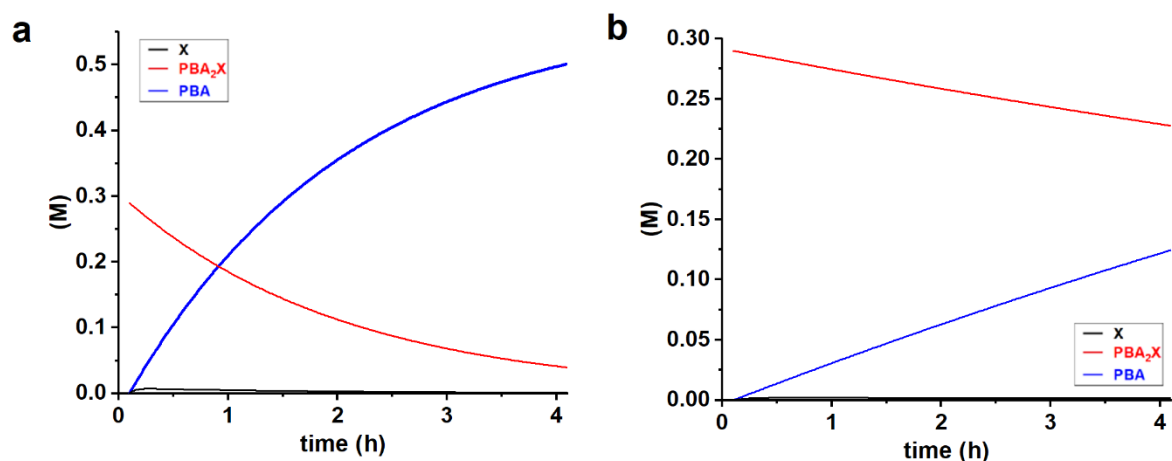
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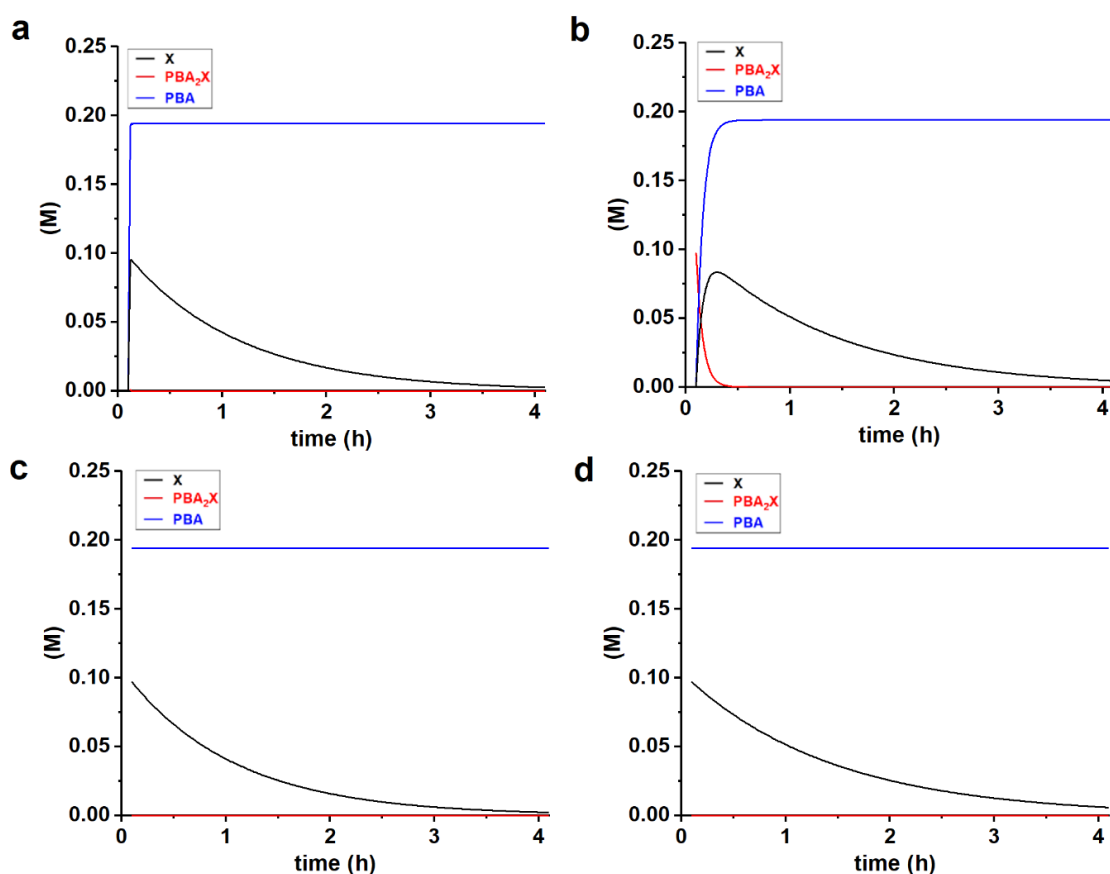
**Figure S1.** Xylose-to-furfural selectivity (mol%) and xylose conversion *versus* time. Reactions performed in a 1:1 toluene-water (pH = 1) biphasic system at 200 °C starting from free xylose in the aqueous phase, at ionic strengths of 0.1 M with (a) no added PBA and (b) 640 mM PBA in the organic phase, and of 3.1 M with (c) no added PBA and (d) 640 mM PBA in the organic phase. (e) Reaction performed in a 1:1:1 toluene-sulfolane-water (pH = 1) system at 180 °C. (f) Reaction performed in a 40:1 dioxane-water monophasic system ([H<sup>+</sup>] = 0.1 M), starting from PBA<sub>2</sub>X (290 mM), at 200 °C.



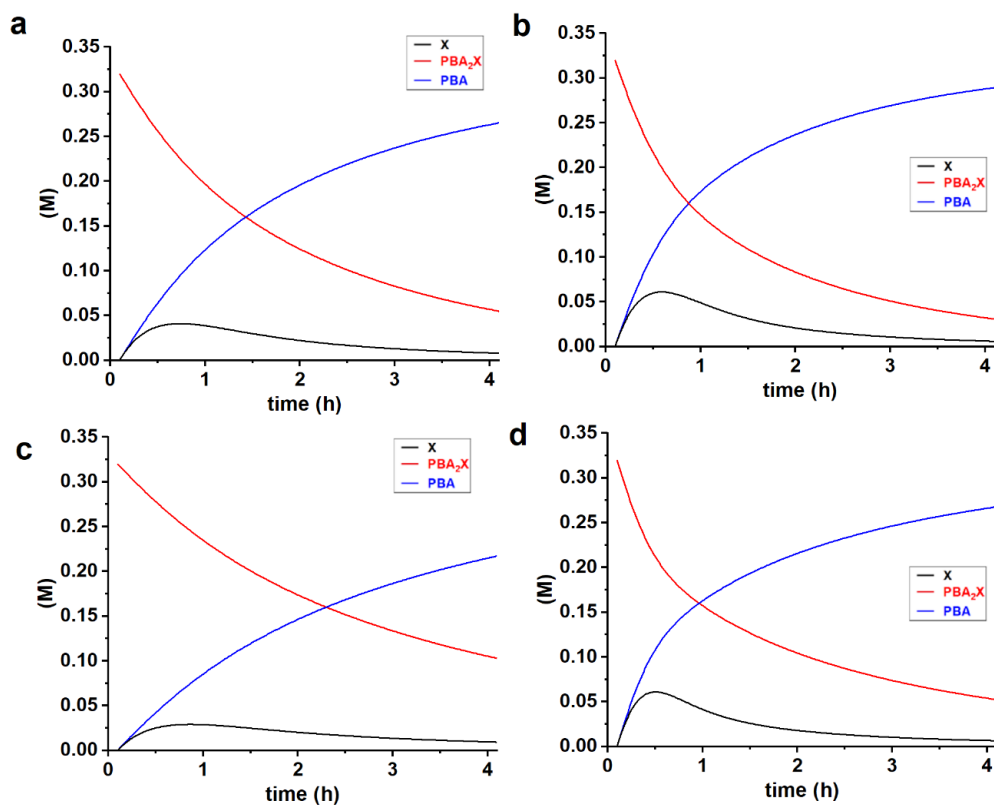
**Figure S2.** Xylose-to-furfural selectivity (mol%) *versus* xylose conversion. Reactions performed in a 1:1 toluene-water (pH = 1) biphasic system at 200 °C starting from free xylose in the aqueous phase, at ionic strengths of 0.1 M with (a) no added PBA and (b) 640 mM PBA in the organic phase, and of 3.1 M with (c) no added PBA and (d) 640 mM PBA in the organic phase. (e) Reaction performed in a 1:1:1 toluene-sulfolane-water (pH = 1) system at 180 °C. (f) Reaction performed in a 40:1 dioxane-water monophasic system ( $[H^+] = 0.1 M$ ), starting from PBA<sub>2</sub>X (290 mM), at 200 °C.



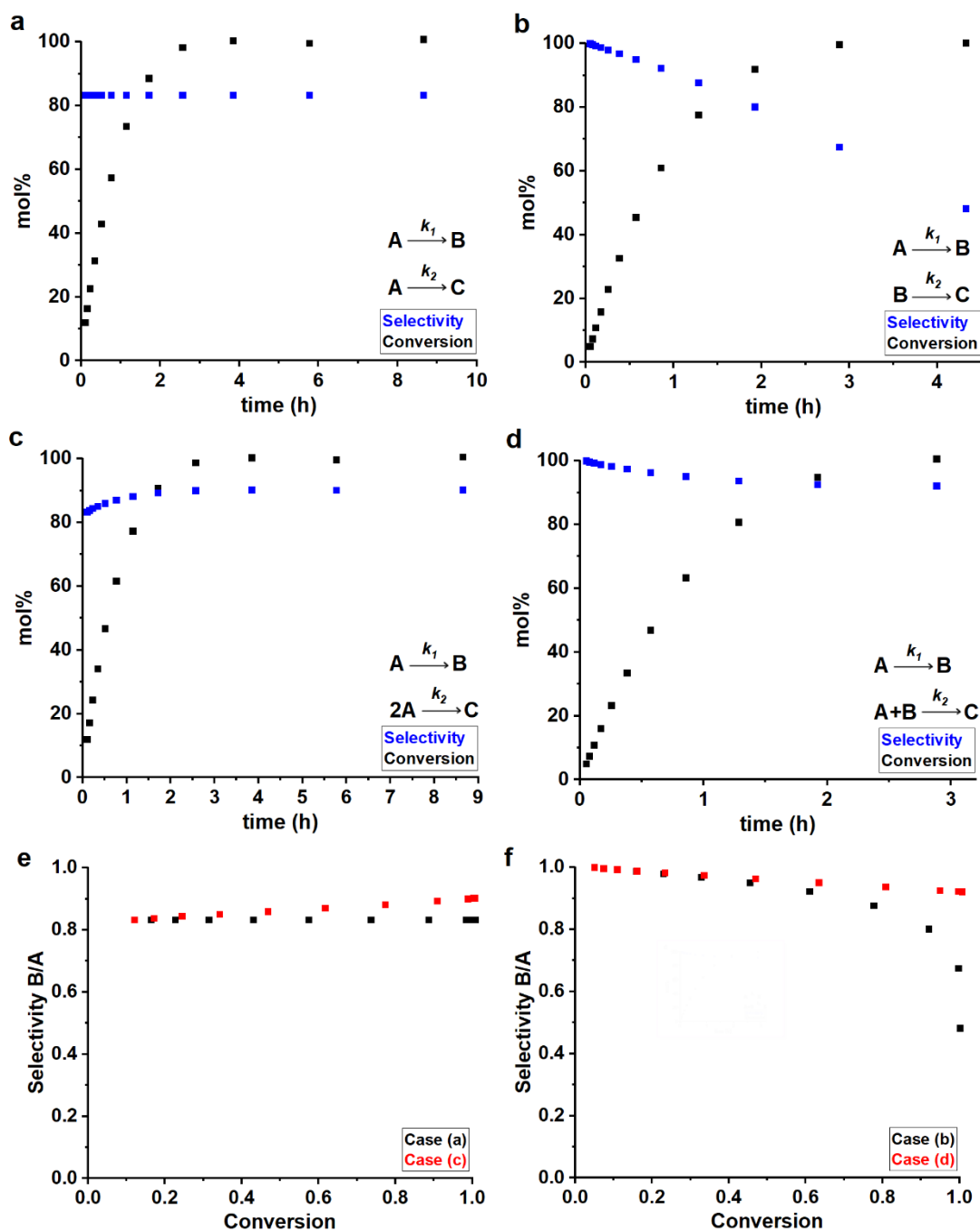
**Figure S3.** Comparison of simulated concentrations for xylose, PBA and PBA<sub>2</sub>X *versus* time, using rate constants given in Table 1 (main text) for the reaction of dehydration performed starting from PBA<sub>2</sub>X at 200 °C, [H<sup>+</sup>] = 0.1 M in a dioxane-water monophasic system at (a) 20:1 v/v ratio or a (b) 40:1 v/v ratio.



**Figure S4.** Comparison of simulated concentrations for xylose, PBA and PBA<sub>2</sub>X *versus* time, using rate constants given in Table 2 (main text) for the reaction of dehydration performed at 180 °C in a (a, c) 1:1:1 v/v/v toluene-sulfolane-water (pH = 1) or a (b, d) 1:1:1 v/v/v MN-sulfolane-water (pH = 1) three-solvent system, starting from either (a, b) 97 mM of PBA<sub>2</sub>X or (c, d) 97 mM of free xylose, in presence of 193 mM of free PBA.



**Figure S5.** Comparison of simulated concentrations for xylose, PBA and PBA<sub>2</sub>X versus time, using rate constants given in Table 3 (main text) for the reaction of dehydration performed starting from PBA<sub>2</sub>X in the organic phase, at 200 °C, pH = 1 and  $I = 3.1$  M in a (a, b) 1:1 toluene-water biphasic system or (c, d) 1:1 MN-water biphasic system, and applying (a,c) no stirring or (b,d) heavy stirring.



**Figure S6.** Comparison between the selectivity profile and the conversion of A for various mechanisms of subsequent and parallel production/degradation. In all cases the two constant  $k_1$  and  $k_2$  are set as 1 and 0.2 respectively. (a) Describes parallel reactions, both first order in A, this results in a flat profile which in this case is at a selectivity of 83%. (b) Describes subsequent reactions, with a progressively decreasing selectivity. (c) Describes parallel reactions, one first order in A and one second order in A, which results in a flat profile after a short increase in the selectivity, limited in the early stages of the reaction. (d) Describes a scenario where there is a reaction between A and B, which results in a flat profile after a short decrease in the selectivity, limited in the early stages of the reaction. (e) and (f) compare the B/A selectivity vs conversion for the cases of parallel reaction (case a and case c) and the cases of subsequent reaction (case b and case d), respectively.

### Degradation first order kinetics in xylose

The first scenario assumes the reaction of by-products formation to be first order in xylose, the second scenario assumes a reaction which is second order in xylose.

In the first scenario  $k_{2f}$  is defined as  $k_{2f} = S_{avg} k_2$ , where  $S_{avg}$  is the average selectivity over the conversion window. Hence,  $k_{2d}$  can be obtained by subtracting  $k_{2f}$  from  $k_2$ . This means that Equation (2) in the main text can be rewritten as Equation (S1).

$$\frac{d[X]}{dt} = k_{1h}[PBA_2X] - k_{1e}[X][PBA]^2 - k_{2f}[X] - k_{2d}[X] \quad (S1)$$

The resulting values are reported in Table 4.

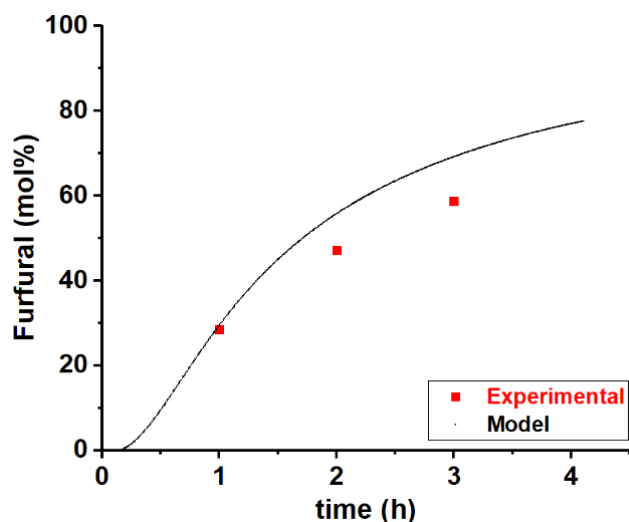
**Table S1.** Values of  $k_2$ ,  $k_{2f}$  and  $k_{2d}$  for the different scenarios at biphasic conditions and different ionic strengths.

Stirring	$I$ (M)	Solvent	Source	$S_{avg}$ (mol%)	$k_2$ (h <sup>-1</sup> )	$k_{2f}$ (h <sup>-1</sup> )	$k_{2d}$ (h <sup>-1</sup> )
regular	0.1	toluene	X (no PBA)	67 ± 2	1.6	1.1	0.54
regular	0.1	toluene	X (PBA)	67 ± 2	1.6	1.1	0.54
regular	0.1	toluene	PBA <sub>2</sub> X	63 ± 3	1.6	1.0	0.60
regular	3.1	toluene	X (no PBA)	76 ± 2	2.8	2.1	0.69
regular	3.1	toluene	X (PBA)	74 ± 2	2.8	2.1	0.69
no	3.1	toluene	PBA <sub>2</sub> X	91 ± 2	2.8	2.6	0.25
regular	3.1	toluene	PBA <sub>2</sub> X	86 ± 1	2.8	2.4	0.39
heavy	3.1	toluene	PBA <sub>2</sub> X	72 ± 1	2.8	2.0	0.79
no	3.1	MN	PBA <sub>2</sub> X	75 ± 3	2.8	2.1	0.72
regular	3.1	MN	PBA <sub>2</sub> X	73 ± 1	2.8	2.0	0.77
heavy	3.1	MN	PBA <sub>2</sub> X	74 ± 2	2.8	2.1	0.74

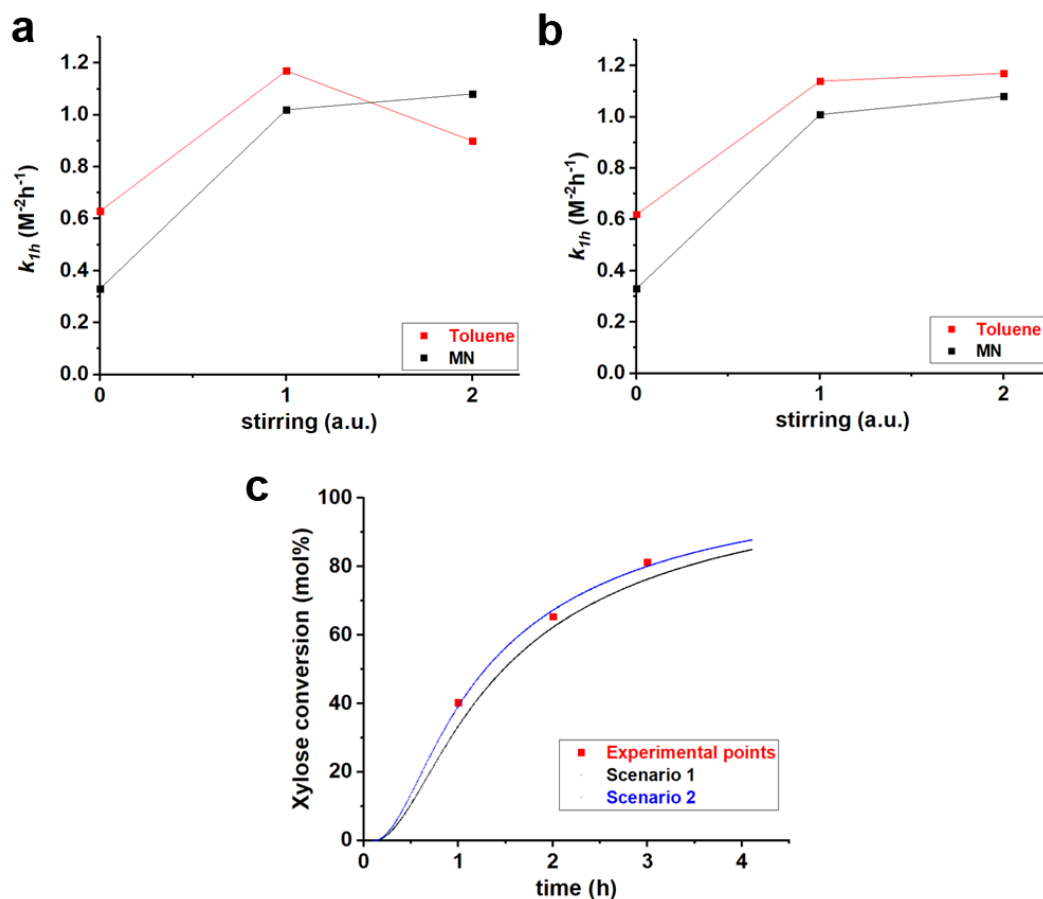
This analysis shows that moving from low to high ionic strength in a toluene-water biphasic system results in an overall increase in the rate of furfural formation. Specifically,  $k_{2f}$  increases by a factor of approx. 2, both when starting from free xylose and from PBA<sub>2</sub>X. At the same time, the changes in  $k_{2d}$  look small, possibly within experimental error, when starting from free xylose. This change in the relative rates leads to the approx. 10 mol% xylose-to-furfural selectivity increase. However, when starting from PBA<sub>2</sub>X, the even higher selectivity requires the rate of by-products formation to drop almost by half when increasing the ionic strength. This is in line with the effect of salt on the partitioning of furfural and PBA<sub>2</sub>X (see above) causing the further enhanced selectivity. Specifically, when the sugar does not start as part of the aqueous phase, the rate of the formation of by-products is lower.

The overall rate of xylose conversion, using PBA<sub>2</sub>X as a starting material, was strongly affected by the stirring speed (Figure 5). In the case of toluene, an increase in stirring rate results in a drop in selectivity that implies a decrease in  $k_{2f}$  (from 2.6 to 2.0) and simultaneous increase in  $k_{2d}$  (from 0.25 to 0.79). Surprisingly, however, no change in selectivity and, thereby, in  $k_{2f}$  and  $k_{2d}$  is observed for MN as extraction solvent. In the case of heavy stirring in toluene, a peak in the <sup>1</sup>H-NMR spectrum (approx. 9-10 ppm) indicates the presence of oxidized species (*e.g.*, carboxylic acids) which are not present in any of the other cases. Further analysis is needed to characterize the nature of these side products and their origin.





**Figure S7.** Comparison between the furfural production predicted by the model and the experimental points for the case of PBA<sub>2</sub>X dehydration in a 1:1 toluene-water (pH = 1) biphasic system at 200 °C at heavy stirring.



**Figure S8.** Comparison between the trend for  $k_{1h}$  comparing no stirring, regular stirring and heavy stirring (arbitrarily assigned values of 0, 1, and 2, respectively) for the fit (a) including and (b) excluding the experimental values of furfural production in the case of heavy stirring in the toluene-water biphasic system. Panel (b) shows that excluding those values result in an agreement in the trends in toluene and MN. Additionally, (c) shows that the fitting of the values of xylose conversion is better when the values are excluded from the fitting (blue curve).

### $k_{2f}/k_{2d}$ Constant

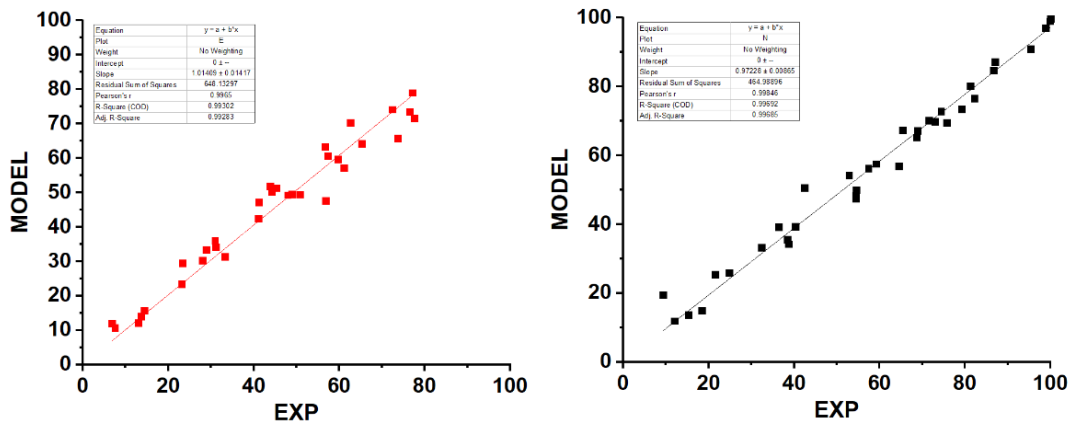
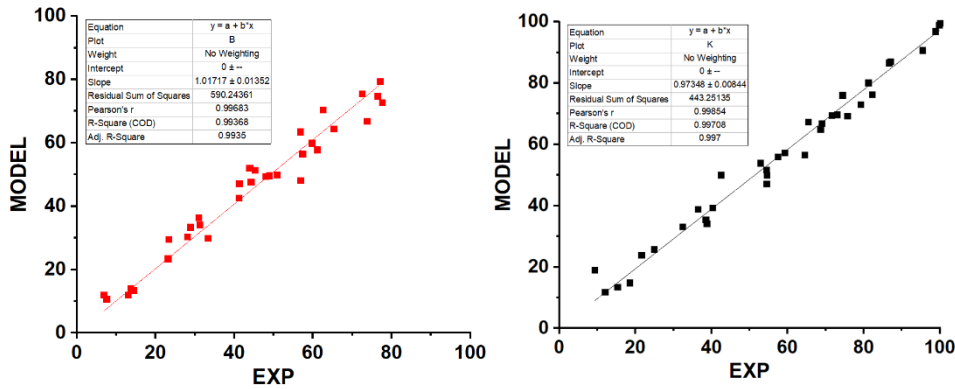


Figure S9. Parity plots for furfural yield (in red) and xylose conversion (in black) for the scenario described in the main text.

### $k_{2d}$ constant



### $k_{2f}$ and $k_{2d}$ unrelated

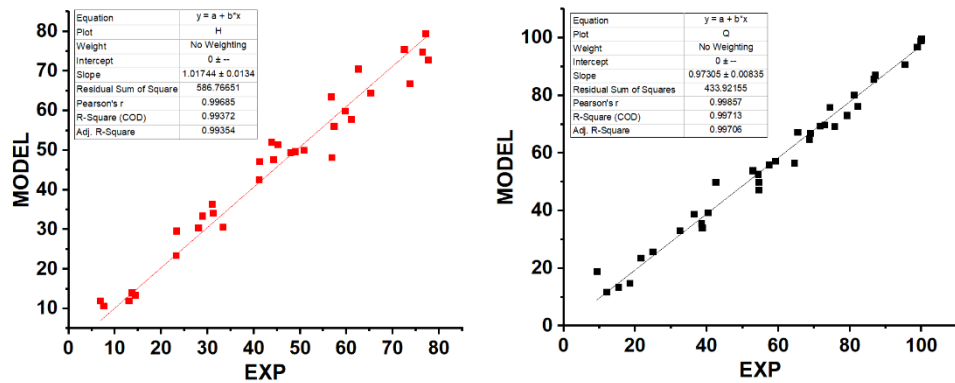


Figure S10. Parity plots for furfural yield (in red) and xylose conversion (in black) for the scenarios described in the main text.

Table S2. Linear regression for the parity plots in Figures S9 and S10.

	Slope furfural	R <sub>2</sub> %	Slope xylose	R <sub>2</sub> %
$k_{2d}$ constant	1.02 +/- 0.01	99.36	0.973 +/- 0.008	99.71
$k_{2f}/k_{2d}$ constant	1.01 +/- 0.01	99.30	0.972 +/- 0.009	99.69
$k_{2f}$ and $k_{2d}$ independent	1.02 +/- 0.01	99.37	0.973 +/- 0.008	99.71

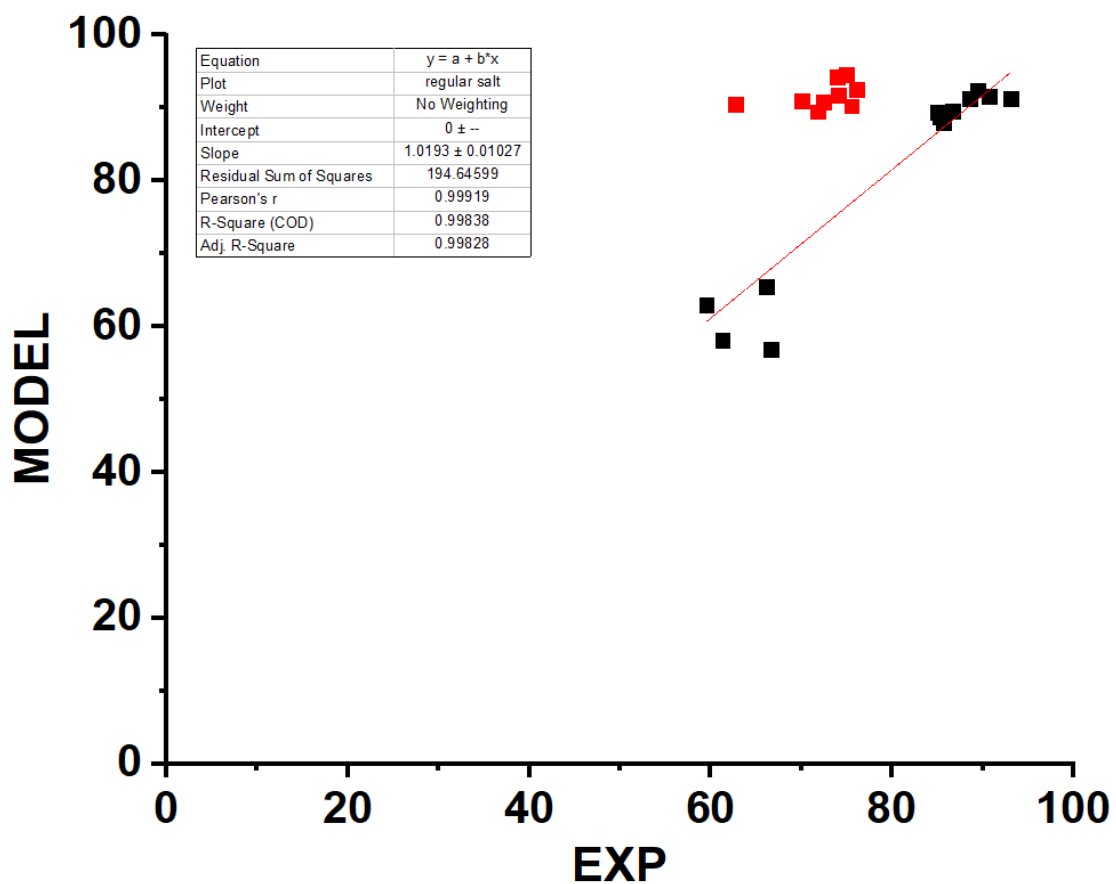
**Table S3.** Fitted values of the kinetic model parameters for the xylose dehydration reaction at 200 °C in a 1:1 toluene-water (pH = 1), biphasic system at different ionic strengths ( $I$ ) and for the xylose dehydration reaction performed at 200 °C at 3.1 M ionic strength in a 1:1 organic-aqueous biphasic system composed of water (pH = 1) and either toluene or MN, at various stirring conditions. This fitting considers a parallel degradation of xylose second order in xylose and a constant  $k_{2d}$  over all the cases.

Stirring	$I$ (M)	Solvent	Source	$k_{1h}$ (h <sup>-1</sup> )	$k_{1e}$ (h <sup>-1</sup> M <sup>-2</sup> )	$k_{2f}$ (h <sup>-1</sup> )	$k_{2d}$ (h <sup>-1</sup> M <sup>-1</sup> )	$K_c$ (M <sup>-2</sup> )
regular	0.1	toluene	X (no PBA)	-	-	0.84	4.51	-
regular	0.1	toluene	X (PBA)	4.70	7.93	0.84	4.51	1.79
regular	0.1	toluene	PBA <sub>2</sub> X	4.70	7.93	0.84	4.51	1.79
regular	3.1	toluene	X (no PBA)	-	-	2.10	4.51	-
regular	3.1	toluene	X (PBA)	1.14	8.96	2.10	4.51	7.92
no	3.1	toluene	PBA <sub>2</sub> X	0.62	4.83	2.10	4.51	7.92
regular	3.1	toluene	PBA <sub>2</sub> X	1.14	8.96	2.10	4.51	7.82
heavy	3.1	toluene	PBA <sub>2</sub> X	1.17	9.18	2.10	4.51	7.82
no	3.1	MN	PBA <sub>2</sub> X	0.33	6.87	2.10	4.51	20.93
regular	3.1	MN	PBA <sub>2</sub> X	1.01	21.14	2.10	4.51	20.93
heavy	3.1	MN	PBA <sub>2</sub> X	1.08	22.53	2.10	4.51	20.93

**Table S4.** Fitted values of the kinetic model parameters for the xylose dehydration reaction at 200 °C in a 1:1 toluene-water (pH = 1), biphasic system at different ionic strengths ( $I$ ) and for the xylose dehydration reaction performed at 200 °C at 3.1 M ionic strength in a 1:1 organic-aqueous biphasic system composed of water (pH = 1) and either toluene or MN, at various stirring conditions. This fitting considers a parallel degradation of xylose second order in xylose and  $k_{2f}$  and  $k_{2d}$  fitted independently over all the cases.

Stirring	$I$ (M)	Solvent	Source	$k_{1h}$ (h <sup>-1</sup> )	$k_{1e}$ (h <sup>-1</sup> M <sup>-2</sup> )	$k_{2f}$ (h <sup>-1</sup> )	$k_{2d}$ (h <sup>-1</sup> M <sup>-1</sup> )	$K_c$ (M <sup>-2</sup> )
regular	0.1	toluene	X (no PBA)	-	-	1.69	17.57	-
regular	0.1	toluene	X (PBA)	1.90	13.04	1.69	17.57	6.86
regular	0.1	toluene	PBA <sub>2</sub> X	1.90	13.04	1.69	17.57	6.86
regular	3.1	toluene	X (no PBA)	-	-	2.10	4.48	-
regular	3.1	toluene	X (PBA)	1.14	8.93	2.10	4.48	7.79
no	3.1	toluene	PBA <sub>2</sub> X	0.62	4.82	2.10	4.48	7.79
regular	3.1	toluene	PBA <sub>2</sub> X	1.14	8.93	2.10	4.48	7.79
heavy	3.1	toluene	PBA <sub>2</sub> X	1.17	9.15	2.10	4.48	7.79
no	3.1	MN	PBA <sub>2</sub> X	0.33	6.86	2.10	4.48	20.90
regular	3.1	MN	PBA <sub>2</sub> X	1.01	21.15	2.10	4.48	20.90
heavy	3.1	MN	PBA <sub>2</sub> X	1.08	22.54	2.10	4.48	20.90

In both cases  $k_{2f}$  increases with ionic strength and  $k_{1h}$  decreases with ionic strength and eliminating stirring. Both in MN and in toluene  $k_{1h}$  stays roughly constant when moving from regular to heavy stirring. Interestingly, when  $k_{2d}$  and  $k_{2f}$  are fitted independently,  $k_{2d}$  decreases with ionic strength, possibly indicating that the presence of salt inhibits the degradation. Further experiments are needed to explore such a theory.



**Figure S11.** Parity plot for xylose-to-furfural production in 1:1 MN-water (in red) and toluene-water (in black) biphasic systems for the dehydration of PBA<sub>2</sub>X performed at 200 °C, with and without salt, at different stirring regimes,  $k_{2f}/k_{2d}$  constant. The same deviation is observed in all the other scenarios.