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

A stepwise kinetic approach to quantify rate coefficients for reactant-, auto- and non-catalyzed urethanization of phenyl isocyanate and 1-butanol

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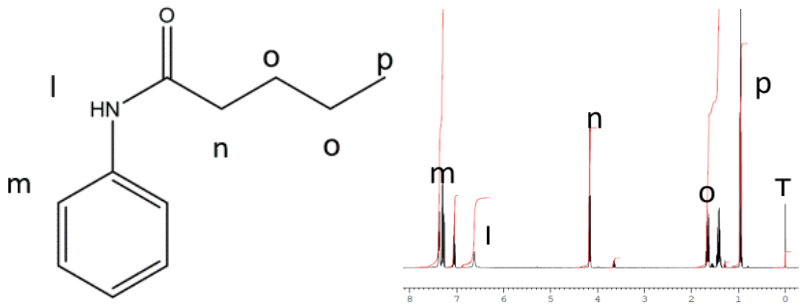
Hendrik Kattner [c] and Dagmar R. D'hooge [a,d]



S1: ^{1}H-NMR spectrum for butyl phenyl carbamate.

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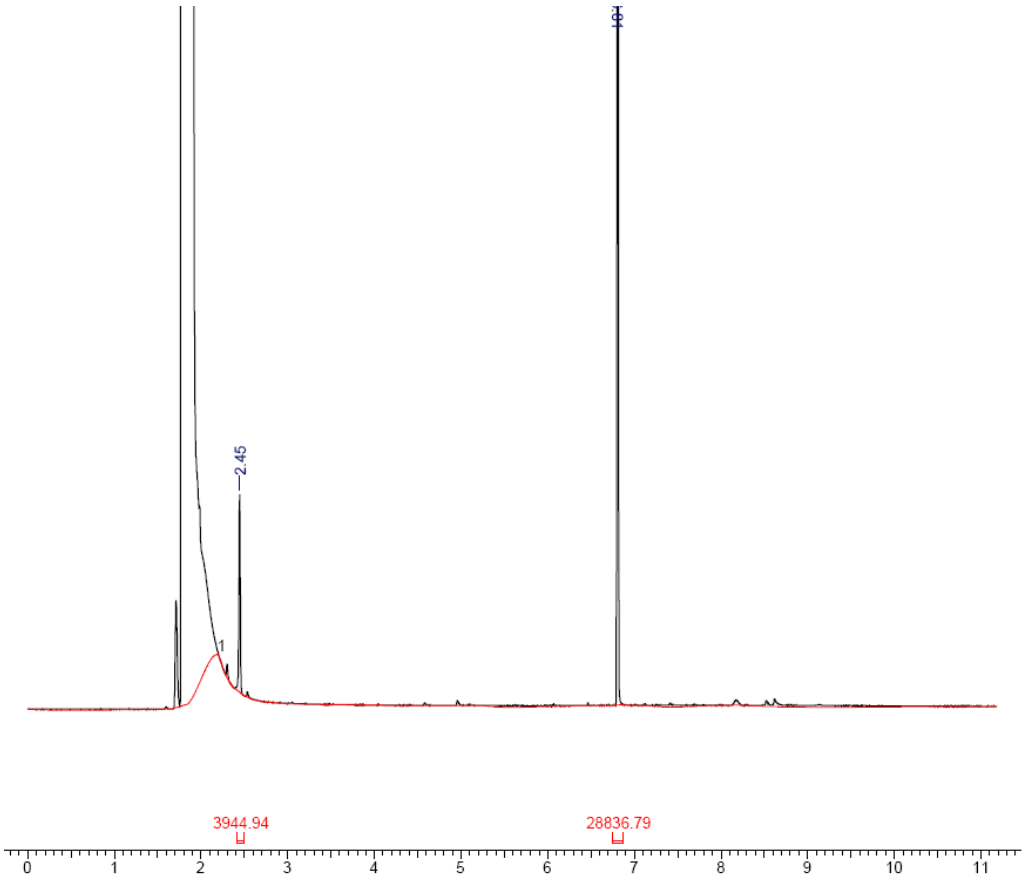

S2: GC chromatogram for butyl phenyl carbamate (6.80 min) and internal standard dichloroethane (2.45 min, added after dissolving pure BPC in dichloromethane).

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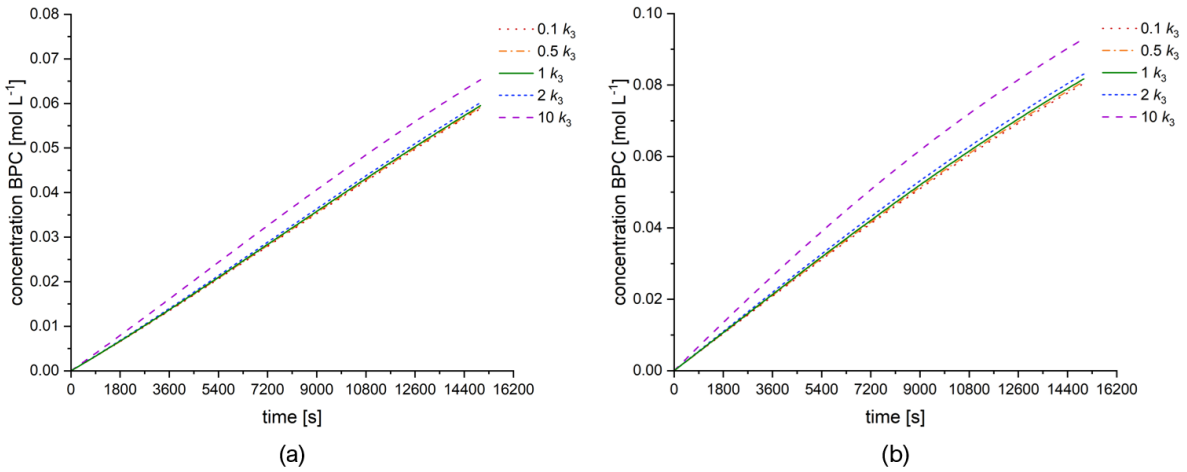
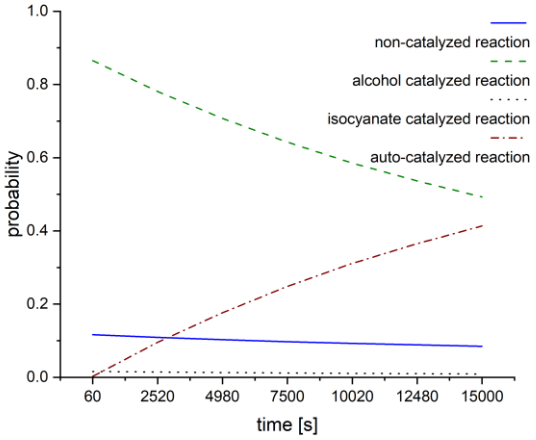
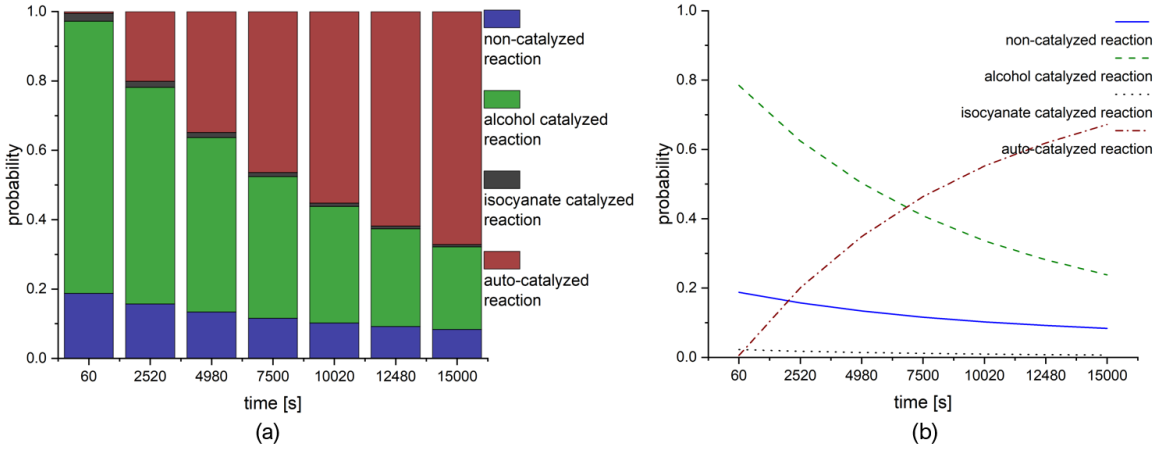


S3: (a) Model sensitivity analysis towards a change in the rate coefficient for the isocyanate catalyzed reaction between PhNCO and 1-BuOH. Respective reference rate coefficients, k values, in Table 5 at 303 K. (b) Model sensitivity analysis towards a change in the rate coefficient for the isocyanate catalyzed reaction between PhNCO and 1-BuOH at a 2 times PhNCO excess. Respective reference rate coefficients, *k* values, in Table 5 at 293 K.



S4: Probabilities of the reaction pathways 1, 2, 3 and 4 in Table 4 at 7 reaction times, according to the values in Table 5 at 293 K and employing an initial concentration of 1.8 10^{-1} mol L^{-1} for both 1-BuOH and PhNCO. For the reference (tuned) parameters in this table the alcohol catalysis (green bar) is always dominant but at higher reaction times the contribution of the carbamate catalysis is very similar in importance, line plot.



S5: Probabilities of the reactions 1, 2, 3 and 4 in Table 4 at 7 reaction times, according to the values in Table 5 at 303 K and employing an initial concentration of 1.8 10^{-1} mol L^{-1} for both 1-BuOH and PhNCO. For the reference (tuned) parameters in this table the alcohol catalysis (green bar) is always dominant but at higher reaction times the contribution of the carbamate catalysis becomes higher, bar (a) and line plot (b).

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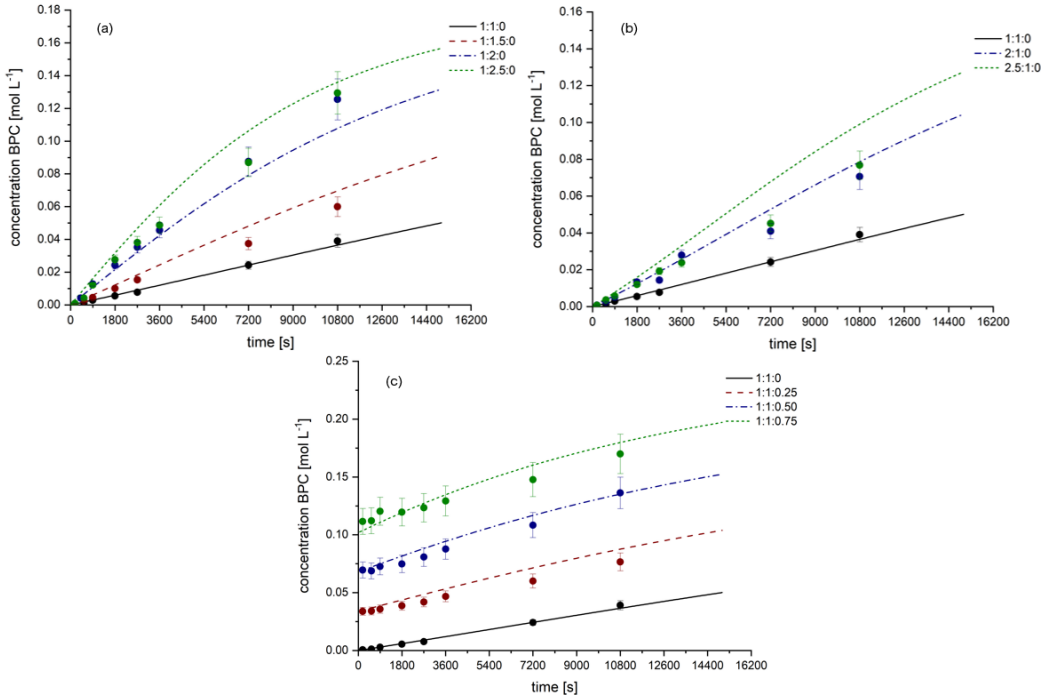
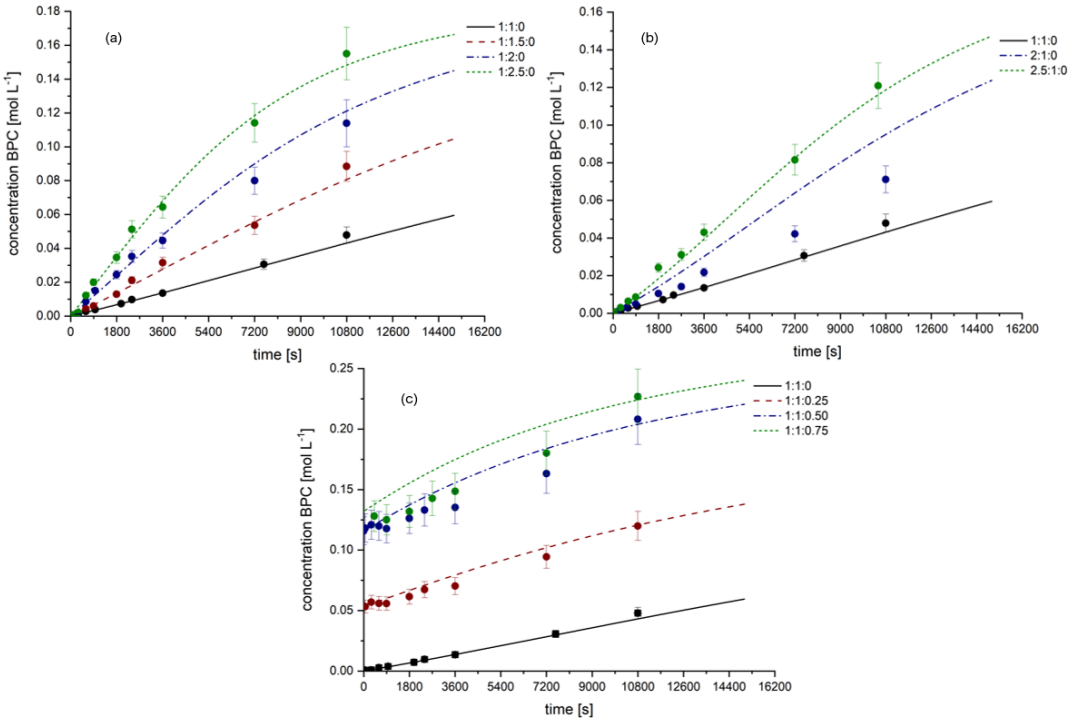
Experimental (●) and modelling (-) data for variable initial butanol concentrations (a), variable initial PhNCO concentrations (b), and variable initial carbamate concentrations (c) at 300 K.



Experimental (●) and modelling (-) data for variable initial butanol concentrations (a), variable initial PhNCO concentrations (b), and variable initial carbamate concentrations (c) at 303 K.



S6: Data comparison at other temperatures.

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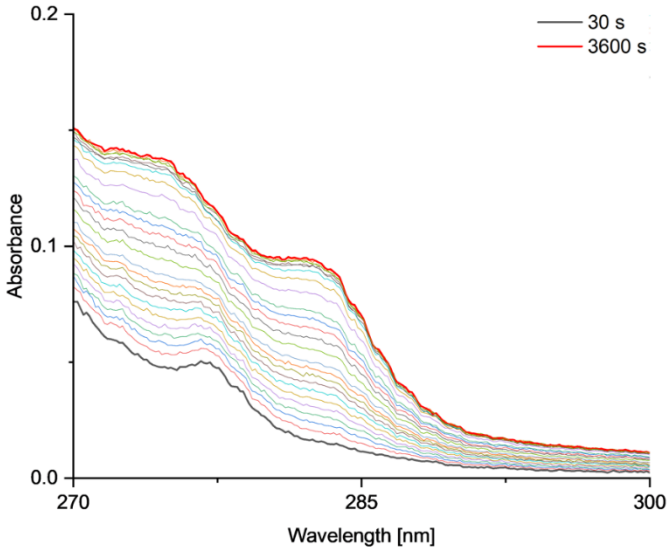
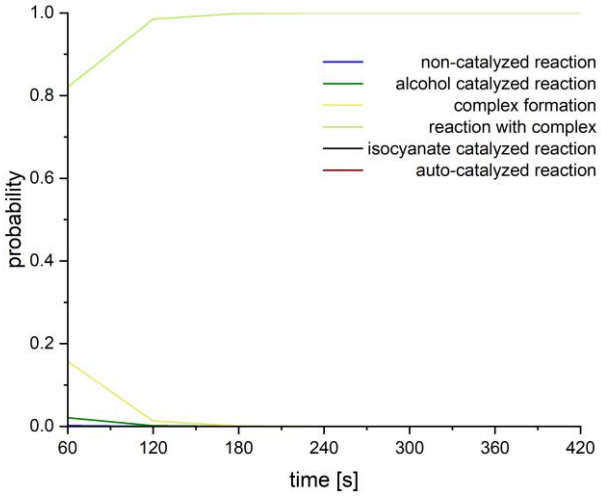


S7: UV-VIS spectra at different times during the urethane formation at large alcohol excess (2ml) ranging from 30 s to 3600 s.



S8: Probabilities of the reactions in Table 4 at 7 reaction times, according to the values in Table 5 at 293 K, with same initial concentrations as in Figure 8a, line plot.

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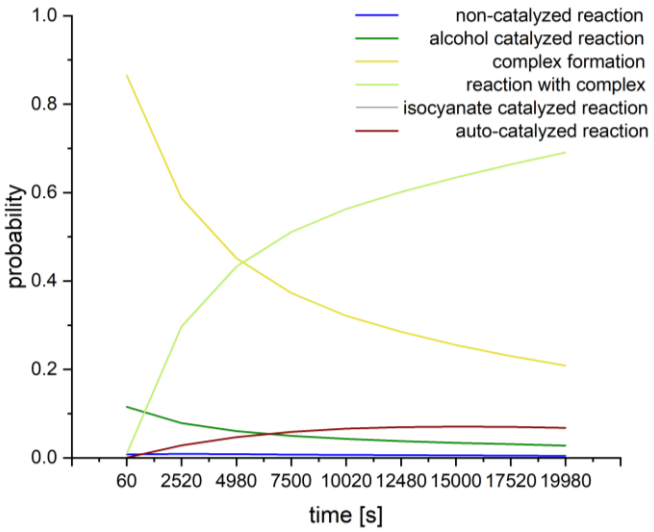

S9: Probability of the reactions from the extended model at low and nearly stoichiometric concentrations, initial BuOH concentration of 3.72 10^{-1} mol L^{-1} and an initial PhNCO concentration of 1.83 10^{-1} mol L^{-1}, line plot.

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