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

Characterization of reaction enthalpy and kinetics in a microscale flow platform

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Supplementary Information

Contents

Chemicals

For the **hydrolysis** experiments an Ac_2O starting solution was prepared by combining Ac_2O (Sigma-Aldrich, ReagentPlus, ≥ 99 wt-%) with AcOH (Alfa Aesar, glacial, 99+ wt-%) at a ratio of $3:1$. Water was used as a second reagent. The water used in this work was purified by the Milli-Q Integral system of Merck with a resulting puritiy of $10-15$ MΩcm.

Teflon block

The inlet block consists of two parts: an aluminum housing with through-holes for the cooling liquid and a Teflon insert with channels for the reagent streams. The Teflon insert is held in place with two screws. IDEX fittings are used to press Teflon tubing against the Teflon insert, so that reactant stream does not come into contact with metal (openings for the fittings are located on the bottom of the aluminum block, see drawings in Fig. S1).

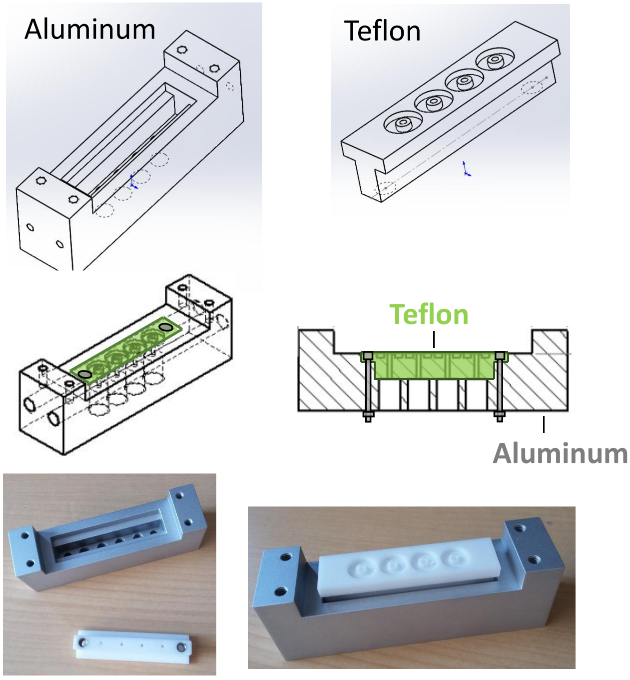

Figure S1 Bottom part of the inlet block consist of an aluminum housing and a Teflon piece for the corrosive reagents. Positions of the inlet and outlet channels are visible in the drawings, as well as through holes for the cooling liquid on the side. Photographs show both parts and their assembly.

IR calibration

Product samples covering a range of conversions were prepared, but as the reaction rate of the hydrolysis of Ac_2O at room temperature is still fairly high and the reaction will start as soon as the reagents mix, special procedure was developed. Both the Ac_2O mixture and water were put into an ice bath after preparation. The samples were left to adjust temperature for 30 minutes and then the Ac_2O solution was added to water over an ice bath while stirred by a magnetic stirrer. After 30 seconds the sample was analyzed by the FTIR spectrometer.

Fig. S2 shows the recorded spectra sets for the calibration. The FTIR software IC IR 7.0 uses these spectra sets to perform a calibration. For this purpose, the composition of the samples had to be provided and characteristic wavelength areas specified, as a basis for the calibration. The calibration can then be applied to experiments recorded by the software. It will compare each recorded spectrum with the calibration set and determine the concentrations of every specified component.

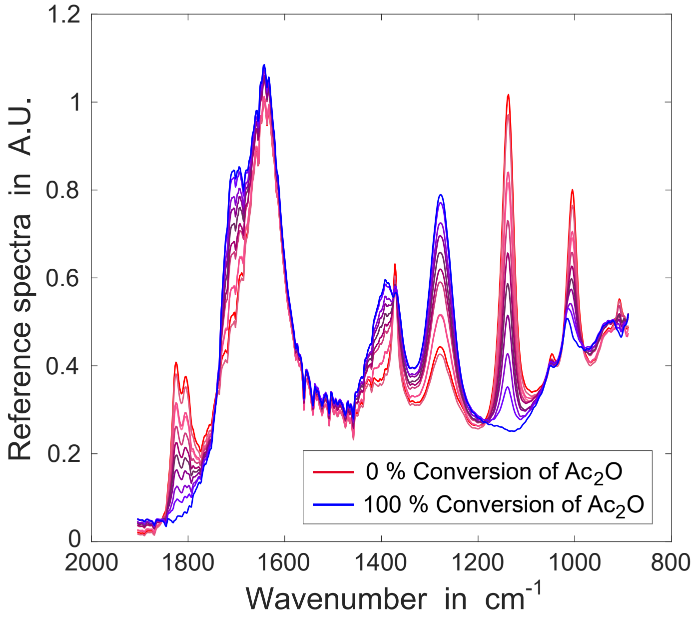

Figure S2 Calibration of FTIR spectrometer: Product samples imitating conversions between 0% (red) and 100% (blue) were prepared and recorded.

Sensible heat of reagents

The influence of the heat capacity of reagents on the baseline signal was investigated experimentally. The heat capacities of the three reagents used in the hydrolysis experiments are stated in Table S1. The heat capacity of the Ac_2O starting solution can be calculated by weighting the component heat capacity by its concentration. This results in a difference in heat capacity of 80.98 $\frac{\mathrm{J}}{\mathrm{molK}}$.

Table S1 Heat capacities of water, Ac_2O and AcOH at 20 °C.[1]

	Water	Ac_2O	AcOH
$C_{p,\,\text{liquid}}$ $\left(\frac{\mathrm{J}}{\mathrm{molK}}\right)$	75.3	168.2	120.5

To check whether the difference between sensible heat of the reagents is detectable, we obtained two baseline signals: one for water and one for acetic anhydride solution. Fig. S3 shows the results of the experiment. A bump in the voltage signal corresponds to hydrolysis occurring between the two reagents when water flow is switched to Ac_2O flow. After all water is removed from the reactor, the new baseline stabilizes at almost the same voltage. The difference was determined to be $\Delta U = 0.1$ mV which lies within the error of a TE measurement. Therefore, the influence of the heat capacity on the TE voltage signal can be neglected. The baseline collection with only one reagent is proven to be viable and water was chosen to be used for the calibration of the TE instead of the reaction mixture.

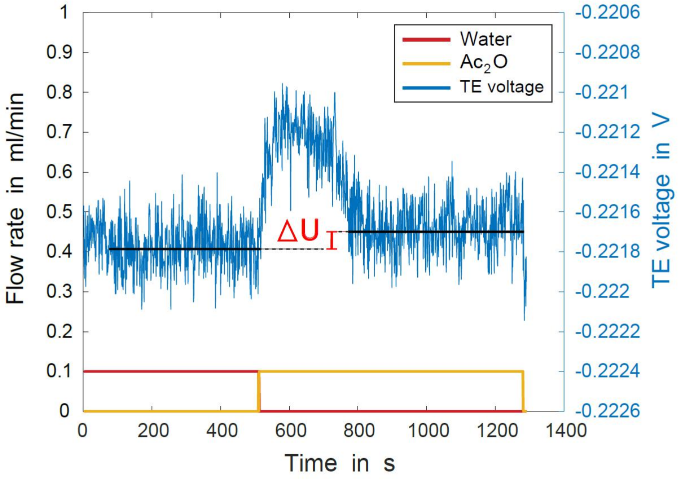

Figure S3 Thermoelectric signal for water and acetic anhydride starting solution. Peak in the middle corresponds to the heat released when switching the reagents.

Theoretical enthalpy values

Enthalpy of a reaction can be predicted using Hess law, by summing up the heat of formation of the reactants and products, with the stochiometric coefficients ν negative for the reactants and positive for the products:

$$\Delta_r H^\circ = \sum_J \nu_J \Delta_f H^\circ(J) \tag{S1}$$

This results in enthalpy of reaction of -58.2 kJ/mol for the hydrolysis of acetic anhydride.

Table S2 Enthalpies of formation, hydrolysis of acetic anhydride.[1]

	Water	Ac_2O	AcOH
$\Delta_f H^\circ \quad (\frac{\mathrm{kJ}}{\mathrm{mol}})$	-285.8	-484.5	-625

Enthalpy values from linear regression

To calculate errors in the values of enthalpy and heat of mixing, data obtained in the experiments was analysed with R software. After performing ordinary least squares regression, confidence intervals and prediction intervals were calculated (Fig. S4).

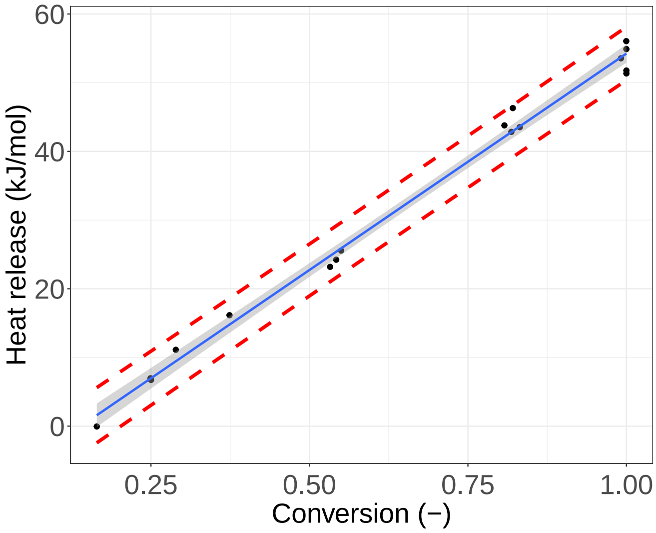

Figure S4 Linear regression (blue line), 95% confidence intervals (gray area) and 95% prediction intervals (red dashed line) of heat released at given conversion for acetic anhydride hydrolysis.

Simple linear regression is expressed using the estimated model coefficients, $\hat{\beta}_0$ and $\hat{\beta}_1$:

$$\hat{y} = \hat{\beta}_0 + \hat{\beta}_1 x \tag{S2}$$

The two estimated coefficients represent the reaction enthalpy (slope $= \hat{\beta}_1$) and the heat of mixing (intercept $= \hat{\beta}_0$). To estimate errors in those two values, the 95% confidence intervals on the estimated model coefficients were computed in R (note that the confidence interval on the estimated coefficient is not equal to the confidence intervals plotted in Fig. S4. For more detailed discussion on the topic see e.g. James et al.[2]). As for the total heat released at full conversion, e.g. the $\hat{y}$ value at $x = conversion = 1$, the error can be determined from the 95% prediction interval, rather than confidence intervals. This is because a prediction made from regressed coefficients should also account for inherent variability of true values around the regression line, and not only for the confidence in the coefficient estimates - this is why prediction intervals are wider than confidence intervals.

Kinetics: comparison with literature

Values of experimentally determined reaction rate constant are displayed against references from literature in Figure S5. Literature values are displayed either as points or lines: points for data available at constant temperature, lines for the reaction rates calculated as a function of temperature via kinetic parameters of the Arrhenius equation. Arrhenius equation is plotted only over the actual temperature range investigated in the corresponding publication, to avoid extrapolation.

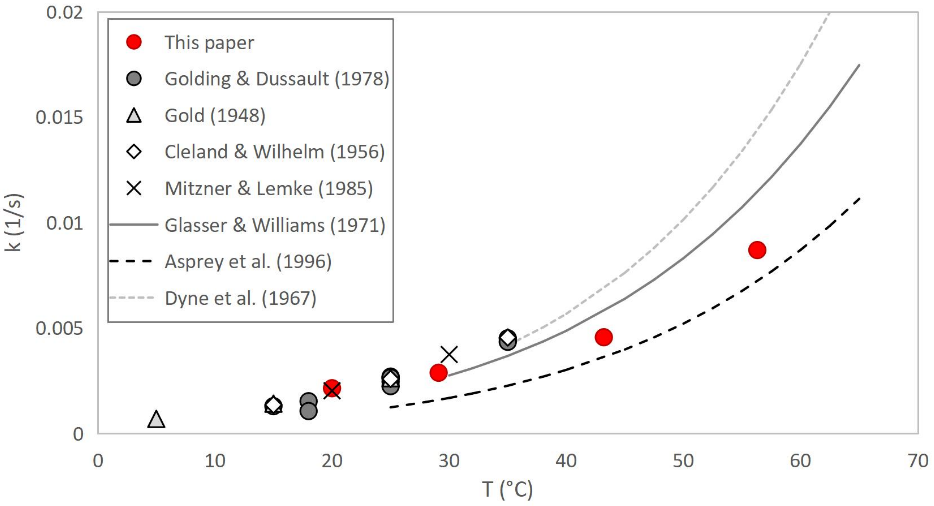

Figure S5 Comparison of pseudo-first order reaction rate constant with literature. Points - values measured at constant temperature, lines - from the kinetic parameters of the Arrhenius equation.[3–9]

Notes and references

[1] D. R. Burgess Jr. Thermochemical Data. In *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*, Eds. P.J. Linstrom and W.G. Mallard. National Institute of Standards and Technology, Gaithersburg MD, 20899.

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