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Reaction Pathways at the Initial Steps of Trioxane Polymerisation

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Supporting information

Deconvolution of time resolved IR spectra

IR spectra were deconvoluted using the software PEAXACT. Single component IR spectra were described with Lorentz functions. Mixture IR spectra were then deconvoluted as linear combination of the single component IR spectra allowing for shift in the band width and position. Developing a calibrated model commenced with making single component models, which shall be described here for the example of acetic anhydride. First, a reference IR spectrum (recorded at the reaction temperature of 0 °C) of acetic anhydride was opened and a certain region for the model was chosen (here 1243 – 890 cm⁻¹; Figure S1).



Figure S1. Reference IR spectrum of acetic anhydride recorded at the reaction temperature of 0 $^{\circ}\text{C}.$

Using the software Lorentz peaks were added and tuned to the single compound model that is denoted in Figure S2. Target was to add as few Lorentz functions as possible to prevent generating an over-determined model. The accuracy of the model was checked with the residuals of the difference between reference spectra and the single component model.



Figure S2. Single compound model of the reference IR spectrum of acetic anhydride recorded at the reaction temperature of 0 $^{\circ}{\rm C}.$

The single component models for all occurring compounds were merged into one combined model (Figure S3).



Figure S3. Merging the single component models for all occurring compounds into a combined model.

The combined model was afterwards calibrated with the IR spectra of concentration series of the reference compounds and mixtures of trioxane and acetic anhydride. The accuracy of the model was evaluated with the identity plots of the predicted against the true concentration value of the samples for the different components and compared between the different models. The plots are shown in Figures S4 – S8.



Figure S4. Evaluating the accuracy of the model with identity plots of the predicted concentration against the true concentration.



Figure S5. Evaluating the accuracy of the model with identity plots of the predicted concentration against the true concentration.



Figure S6. Evaluating the accuracy of the model with identity plots of the predicted concentration against the true concentration.



Figure S7. Evaluating the accuracy of the model with identity plots of the predicted concentration against the true concentration.



Figure S8. Evaluating the accuracy of the model with identity plots of the predicted concentration against the true concentration.

Time-concentration profile of the oligomerisation reaction

Time-concentration profiles were recorded as detailed in the main text. Intervals with systematic errors in the profiles of acetic anhydride or TOD resulting from overlapping bands in the IR spectra were dismissed for further interpretation. In some instances, the bands for DOD and MOD were not observed in the time-resolved IR spectra yet detected in the liquid fraction suggesting a concentration below the detection limit.



Figure S9 Time-resolved IR spectra of the carbonyl region for the oligomerisation of trioxane in the presence of acetic anhydride (3:1)

Deconvolution of ¹H NMR spectra

To determine the composition of the soluble fraction ${}^{1}H$ – and ¹³C-APT – NMR – as well as Heteronuclear Single Quantum Correlation (HSQC) - and Heteronuclear Multibond Correlation (HMBC) – 2D NMR experiments were performed. The HSQC spectrum of the oxymethylene diacetate mixture is depicted in Figures S2-S4 and the ${}^{1}H \rightarrow {}^{13}C$ single bond coupling of the acetate methyl groups (1.95-2.10 ppm $\rightarrow 20.8$ ppm, green circle, Figure S10 and Table S1) and the oxymethylene groups (grey circles, Figure S10 and Table S1) are highlighted. Multibond couplings of the ¹³C NMR signals at 174.6, 170.4, 170.3, 170.1 and 169.6 ppm assigned to the carbonyl moieties to the 1H NMR signals assigned to the acetate methyl groups (1.95-2.10 ppm, green ovals, Figure S10) and to the oxymethylene groups (5.65, 5.29 and 5.27 ppm, grey ovals, Figure S10 and Table S1) were observed. This shows that the soluble fraction was composed of acetate capped oxymethylene chains. The oxymethylene group with a ¹H NMR signal at 5.65 ppm (¹³C NMR signal: 79.1 ppm) showed a single coupling to a ¹³C NMR signal of a carbonyl group at 170 ppm. This means that this signal can be assigned to monooxymethylene diacetate (Figure S10).



¹H Chemical shift [ppm]

¹H Chemical shift [ppm]

Figure S10 Oligomerisation of trioxane in the presence of acetic anhydride as chain transfer agent and triflic acid as catalyst at 0 °C (top). The ${}^{1}H - {}^{13}C -$ coupling of protons and their neighbouring carbons were determined with HSQC – 2D – NMR spectroscopy and are highlighted with coloured circles (green: methyl groups of the acetates, grey: methylene groups of the oxymethylene units). The multi bond couplings of those moieties to neighbouring carbonyl groups were determined with HMBC – 2D – NMR spectroscopy and are highlighted with coloured ovals (green: methyl groups of the acetates, grey: methylene groups of the oxymethylene units).

Further, multibond couplings of ester bound oxymethylene units (5.29 and 5.27 ppm) to other oxymethylene units were observed (Figure S11).



Figure S11 Assignment of ¹H and ¹³C NMR signals to oxymethylene segments of different length (coloured circles). Multi bond couplings between the different oxymethylene units were determined with HMBC – 2D – NMR spectroscopy and are highlighted with coloured ovals. *Pseudo signals of carbon isotopes.

The multibond coupling and the assignment of ¹H to ¹³C NMR signals of the oxymethylene units are listed in Table S1. The ¹H NMR signal observed at 5.29 ppm (¹³C NMR signal 86.8 ppm) was observed to couple only to an oxymethylene group in the same chemical environment. Thus, the ¹H NMR signals at 5.29 ppm were assigned to dioxymethylene units (Table S1). Further couplings between ¹H NMR signals at 5.27 ppm and ¹³C NMR signals at 92.3 ppm (¹H NMR signal at 4.87 ppm) as well as 90.7 & 90.6 ppm (¹H NMR signal at 4.85 & 4.84 ppm) were observed. The signal at 4.87 ppm (¹H NMR) was observed to only couple back to signal (¹H NMR signal: 5.27 ppm, ¹³C NMR signal: 85.5 ppm) of the ester bound oxymethylene unit. This means that the ¹H NMR signal at 4.87 ppm can be assigned to the inner shell oxymethylene unit of a three oxymethylene unit long oxymethylene segment. The ¹H NMR signals at 4.84 ppm was found to couple to ¹³C NMR signals at 85.5 ppm (¹H NMR signal at 5.26 ppm) and to 89.2 ppm (¹H NMR signal at 4.82 ppm). Thus, the ¹H NMR signal at 4.89 ppm can be assigned to the third oxymethylene shell, which are connected to a fourth shell. Furthermore, the ¹³C NMR signals at 89.3, 89.2 and 89.1 ppm (1H NMR signals at 4.82, 4.82 and 4.81 ppm) was observed to couple with ¹H NMR signals at 4.84 ppm (¹³C NMR signals at 90.7 & 90.6 ppm) and to 4.81 ppm (¹³C NMR signal at 89.1 ppm). Thus, the ¹H NMR signals at 4.82 ppm can be assigned to a fourth shell of oxymethylene signals. Moreover, the coupling to the ¹³C NMR signal indicates that further oxymethylene units (fifth shell) can be found at the same chemical shift (4.81 ppm). This means that ¹H NMR signals were assigned to specific chains: monooxymethylene - (5.65 ppm), dioxymethylene - (5.29 ppm), trioxymethylene - (4.87 ppm), quatrooxymethylene -(4.85 ppm) and pentaoxymethylene diacetate (4.82 ppm). Noteworthy, only the signal of monooxymethylene diacetate was well separated, while the other signals were overlapping.

Table S1 Overview of multibond and single quantum correlations of ¹³C and ¹H NMR signals observed in HSQC and HMBC NMR experiments performed for the obtained oligooxymethylene diacetate mixture.

HSQC ^a		HMBC ^b	HSQC ^a	
¹³ C NMR	¹ H NMR		¹ H NMR	¹³ C NMR
signal [ppm]	signal [ppn	1]	signals	signals [ppm]
			[ppm]	
79.1	5.76	\rightarrow	-	170.2
86.8	5.37	\rightarrow	-	170.2
86.8	5.37	\rightarrow	5.37	86.8
85.5	5.36	\rightarrow	-	170.2
85.5	5.36	\rightarrow	4.92	92.3
85.5	5.36	\rightarrow	4.89	90.6
92.3	4.92	\rightarrow	5.36	85.5
90.6	4.89	\rightarrow	5.36	85.5
90.6	4.89	\rightarrow	4.87	89.2
89.2	4.87	\rightarrow	4.87	89.2
89.2	4.87	\rightarrow	4.89	90.6

^a Heteronuclear Single Quantum Correlations (HSQC) between carbons and their neighbouring protons, ^b Heteronuclear Multi Bond Correlation of carbons and protons to protons and carbons of neighbouring moieties.

The composition of oxymethylene diacetate mixtures was determined by deconvolution of their respective ¹H-NMR spectra. TOPSPIN 3.2 was used to fit of Lorentz/Gauss functions to the measured spectra (Figure S12). The fitted and measured spectra were found to be in good agreement (compare Figure S12, insert right), which allowed to determine integrals of all occurring signals in good quality. The assignment of the signal is shown in Figure S12 for clarity (insert left).



Figure S12 Deconvolution of ¹H-NMR signals shown for the oxymethylene region of liquid fraction. Overlay of modelled and measured ¹H-NMR spectra of the liquid fraction (insert right). Assignment of oxymethylene signals to structural units (insert left).

The integrals of signals at chemical shifts of 5.66 (monooxymethylene diacetate, MOD), 5.29 (dioxymethylene diacetate, DOD), 4.87 (trioxymethylene diacetate, TOD), 4.85 (quatrooxymethylene diacetate, QOD) and 4.82 ppm (pentaoxymethylene diacetate, POD) were used to subtract the respective amounts from the integrals of the signals representing the acetate groups (2.00 ppm) as well as from the outer (5.27 ppm) and inner (4.84 ppm) oxymethylene shells. The remaining values of the oxymethylene and acetate integrals were used to determine the average chain lengths of oxymethylene diacetate chains (n_{long}) longer than n = 5 (Figure

S12). Moreover, the composition of the amounts oxymethylene units in the different chains relative to total amount of oxymethylene and the overall average oxymethylene chain length (n_{avg}) were calculated.

Determination of force constants

The position of stretch and vibrational bands in an infrared spectrum describes the force constant (f) as described by Equation F1, which was derived from the model of the harmonic oscillator.

$$f = (2 \pi v)^2 \mu$$
 F1

The reduced mass (μ) describes the mass centre of a harmonic oscillator according to equation F2.

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$
 F2

As approximation the molecules were treated as a harmonic oscillator with one mass on each side of the bond. The masses (m_1, m_2) were chosen as depicted in Scheme S1.



Scheme S1. Masses for the approximation of a harmonic oscillator were picked with the oxygen atom as center point.

The IR spectra of trioxane, TOD, DOD and MOD were measured as dichloromethane solution at 0 $^{\circ}$ C (*in situ* IR spectroscopy), in order to ensure that the determined force constants are describing the behaviour under reaction conditions.

The position and determined force constant of the symmetrical ether and ester stretch vibrations of trioxane, TOD, DOD and MOD are listed in Table S2.

Table S2. Observed position and determined force constant of the symmetrical ether and
ester stretch vibrations.

	v _{sym} (Ether)	k [N/m]	v _{sym} (Ester)	k [N/m]ª
MOD	-	-	1016	1647
DOD	950	1942	1007	1813
TOD	932	2187	1002	1923
Trioxane	930	943	-	-

^aReduced masses for the ester stretch vibrations were choosen similar to the ones for the ether stretch vibration, but with the ester oxygen always being the center point.

The force constants are a measure for the strength of a bond, as it influences its strength of stretch vibrations.

Time-concentration profiles

The combined model was used to determine time-concentration profiles (Figure S9 – 16) for the time resolved *in situ* IR spectra. The displayed profiles were normalised on the starting amount of trioxane. Acetic anhydride and trioxane were converted fast in the initial phase of reaction catalysed with trifluoromethane sulfonic acid. In parallel, TOD was formed quickly, while DOD and MOD were formed more slowly. The concentrations of acetic anhydride and TOD decreased slowly, once trioxane was fully (within 200 seconds) converted. In parallel, the concentrations of DOD and MOD was increased in equimolar ratio. The absence of a S-shaped curve for the concentration profiles of DOD and MOD suggests that those can not only be formed as consecutive product of TOD, but also directly from trioxane (Figure S9).



Figure S13. Time-concentration profile of the reaction of trioxane with acetic anhydride catalysed by trifluoromethane sulfonic acid (CH_2Cl_2 , 0 °C).

Acetic anhydride and trioxane were converted fast in the initial phase of reaction catalysed with perchloric acid. In parallel, TOD was formed quickly, while DOD and MOD were formed more slowly. The concentrations of acetic anhydride and TOD decreased slowly, once trioxane was fully converted (within 300 seconds). In parallel, the concentrations of DOD and MOD was increased in equimolar ratio. The S-shaped curve of the concentration profiles for DOD and MOD suggests that those were mainly formed as consecutive product of TOD (Figure S10).



Figure S14. Time-concentration profile of the reaction of trioxane with acetic anhydride catalysed by perchloric acid (CH₂Cl₂, 0 °C).

Acetic anhydride and trioxane were converted fast in the initial phase of reaction catalysed with antimony (III) triflate. In parallel, TOD was formed quickly, while DOD and MOD were formed more slowly. The concentrations of acetic anhydride and TOD decreased slowly, once trioxane was fully converted (within 100 seconds). In parallel, the concentrations of DOD and MOD increased in equimolar ratio. The very high activity of the catalyst did not permit an interpretation of the shape of DOD's and MOD's concentration profile in the initial phase of the reaction (Figure S11).



Figure S15. Time-concentration profile of the reaction of trioxane with acetic anhydride catalysed by antimony (III) triflate (CH_2Cl_2 , 0 °C).

Acetic anhydride and trioxane were converted fast in the initial phase of reaction catalysed with bismuth (III) triflate. In parallel, TOD was formed quickly, while DOD and MOD were formed more slowly. The concentrations of acetic anhydride and TOD decreased slowly, once trioxane was fully converted (within 300 seconds). In parallel, the concentrations of DOD and MOD was increased in equimolar ratio (Figure S12). The *in situ* IR measurement was disturbed by the formation of a layer of a polymeric substance on the IR probe (Figure S13). The *in situ* IR measurement was therefore aborted after 1 hour, while the reaction was kept running to complete the 2 hours of

reaction time. The first 1000 seconds were undisturbed and used for the kinetic modelling.



Figure S16. Time-concentration profile of the reaction of trioxane with acetic anhydride catalysed by bismuth (III) triflate (CH₂Cl₂, 0 °C). The first 1000 seconds were used for the kinetic modelling.



Figure S17. Time-concentration profile of the reaction of trioxane with acetic anhydride catalysed by bismuth (III) triflate (CH_2Cl_2 , 0 °C).

The bismuth (III) triflate catalysed reaction was repeated with a lower catalyst concentration and shorter reaction time, in order to prevent the occurrence of side reactions. Acetic anhydride and trioxane were converted, while TOD was formed in parallel. DOD and MOD were formed much slower in parallel and only comprise 3.3 % (¹H NMR) of the composition of the final product. It was not possible to resolve the low concentrations of DOD and MOD (Figure S14).



Figure S18. Time-concentration profile of the reaction of trioxane with acetic anhydride catalysed by bismuth (III) triflate at a decreased concentration of 0.1 mol-% (CH_2Cl_2 , 0 °C).

Acetic anhydride and trioxane were converted slowly in the initial phase of reaction catalysed with scandium (III) triflate. In parallel, TOD was formed, while DOD and MOD were formed more slowly. The concentrations of acetic anhydride and TOD decreased more slowly, once trioxane was fully (within 3000 seconds) converted. In parallel, the concentrations of DOD and MOD increased in equimolar ratio. Only the beginning of a S-shaped curve for the concentration profiles of the consecutive products DOD and MOD was observed, as those were formed very slowly (Figure S19).



Figure S19. Time-concentration profile of the reaction of trioxane with acetic anhydride catalysed by scandium (III) triflate (CH_2Cl_2 , 0 °C).

Acetic anhydride and trioxane were converted very slowly over the course of reaction catalysed with yttrium (III) triflate. In parallel, TOD was formed. DOD and MOD were detected by the model, even though, not formed in the reaction. This suggests that an unidentified side product was formed (Figure S20).





Using trifluoromethane sulfonic acid as catalyst the concentrations of acetic anhydride and TOD decreased slowly. In parallel equimolar amounts of DOD and MOD were formed. TOD was not fully converted within the reaction time of 2 h (Figure S21).





Determination of kinetic constants

The kinetic model was based on the reactions shown in Scheme S2.



Scheme S2. Reactions considered in the kinetic model for the reaction of trioxane with acetic anhydride.

Time-concentration profiles were fitted with the kinetic model described by equations S1 to S5.

$$\frac{d(Trioxane)}{dt} =$$

$$k_1c(Trioxane)(Ac_20)$$

$$k_2c(Trioxane)(Ac_20)$$
(S1)

$$\frac{d(Ac_2O)}{dt} =$$

$$k_1c(Trioxane)(Ac_2O)$$
(S2)

$$= k_3 c (TOD) (Ac_2 O)$$

$$= d(TOD)$$

$$\frac{dt}{dt} = k_1 c(Trioxane)(Ac_2 0)$$

$$-k_2 c(TOD)(Ac_2 0)$$
(S3)

$$\frac{d(DOD)}{dt} =$$

$$+ k_2 c(Trioxane)(Ac_2 O)$$

$$+ k_2 c(TOD)(Ac_2 O)$$
(S4)

$$\frac{d(MOD)}{dt} =$$

$$+ k_2 c(Trioxane)(Ac_2 0)$$

$$+ k_3 c(TOD)(Ac_2 0)$$
(S5)

The fit of the model is in excellent agreement to the recorded time-concentration profile of the trifluoromethane sulfonic acid catalysed reaction between acetic anhydride and trioxane (Figure S22).





The fit of the model is in good agreement to the recorded timeconcentration profile of the perchloric acid catalysed reaction between acetic anhydride and trioxane. Minor deviations were observed in the concentrations of acetic anhydride and TOD between 200 and 2500 seconds (Figure S23).





The fit of the model is in good agreement with the recorded time-concentration profile of the antimony (III) triflate catalysed reaction between acetic anhydride and trioxane. The start of the reaction was not well resolved, as trioxane was only present in the first three spectra (Figure S24).



Figure S24. Fitted time-concentration profile of the reaction of trioxane with acetic anhydride catalysed by antimony (III) triflate (CH_2Cl_2 , 0 °C).

The data of the bismuth (III) triflate catalysed reaction of acetic anhydride with trioxane was fitted for the first 1000 seconds. The fit is in good agreement with the recorded data. A sideproduct resulted a systematic error at the later stage of the reaction (Figure S25).



Figure S25. Fitted time-concentration profile of the reaction of trioxane with acetic anhydride catalysed by bismuth (III) triflate (CH_2Cl_2 , 0 °C).

The fit of the model is in good agreement to the recorded timeconcentration profile of the bismuth (III) triflate (reduced catalyst concentration) catalysed reaction between acetic anhydride and trioxane. The fit was based on second oder in trioxane (Figure S26).



Figure S26. Fitted time-concentration profile of the reaction of trioxane with acetic anhydride catalysed by bismuth (III) triflate at a decreased concentration of 0.1 mol-% (CH₂Cl₂, 0 °C).

The fit is in good agreement to the recorded time-concentration profile of the bismuth (III) triflate (reduced catalyst concentration) catalysed reaction between acetic anhydride and trioxane. The fit was based on second oder in trioxane. Minor deviations are notable between the fit and the experimental data for acetic anhydride and TOD (Figure S27).





The data of the yttrium (III) triflate catalysed reaction of acetic anhydride with trioxane were fitted for the first 3000 seconds. The fit was here in good agreement with the recorded data. A side product resulted in a systematic error at the later stage of the reaction. The concentrations of DOD and MOD were omitted, as DOD and MOD were not found in the final product mixture (Figure S28).



Figure S28. Fitted time-concentration profile of the reaction of trioxane with acetic anhydride catalysed by yttrium (III) triflate (CH_2Cl_2 , 0 °C).

The fit of the model is in good agreement to the recorded timeconcentration profile of the trifluoromethane sulfonic acid catalysed reaction between acetic anhydride and TOD (Figure S29).



Figure S29. Fitted time-concentration profile of the reaction of TOD with acetic anhydride catalysed by trifluoromethane sulfonic acid (CH₂Cl₂, 0 °C).