Supporting Information for:

Revisiting the deoxydehydration of glycerol towards allyl alcohol under continuous-flow conditions

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1. Continuous-flow setups

1.1 Generalities

1.1.1 Pumps

ThalesNano microHPLC® pumps (0.01 – 10 mL min^{-1}, max 80 bar, wetted parts: SS 316, ruby and sapphire) were utilized for the pumping of dynamic reactive feed solutions of (a) glycerol and formic acid; (b) glycerol, formic acid and triethyl orthoformate and (c) glycerol and triethylorthoformate. Alternatively, Chemyx Nexus 6000® High Pressure syringe pumps using Chemyx stainless steel 20 mL syringes equipped with Dupont™ Kalrez® Spectrum™ AS-568 O-rings (0.549 x 0.103") were utilized for the injection of (a) glycerol only or (b) purified **2b/2c** dioxolane/dioxane mixture.

1.1.2 Microfluidic reactor elements

1.1.2.1 SS loops

The microfluidic SS reactors were constructed with deburred-end, steam-cleaned and acid-passivated 316 SS tubing (1.58 mm outer diameter, 500 µm internal diameter) of various internal volumes. Optimized conditions involved a thermolysis loop of 1.6 mL internal volume, and a cooling loop of 0.34 mL internal volume.

1.1.2.2 PEEK tubing

The section connecting the HPLC pump to the check valve upstream the reactor that was not subjected to high temperature was constructed from PEEK tubing (green striped, 1.58 mm outer diameter, 750 µm internal diameter).

1.1.2.3 PFA tubing

The section connecting the BPR to the collection flask downstream the reactor that was not subjected to high pressure and temperature was constructed from PFA tubing (high purity PFA; 1.58 mm outer diameter, 750 µm internal diameter).

1.1.2.4 Connectors, ferules and mixers

Sections of the reactor that were not subjected to high temperature were equipped with coned PEEK fittings (one-piece Fingertight Long, PEEK, 10-32 Coned, for 1/16" OD tubing from IDEX/Upchurch). Sections of the reactor that were subjected to high temperature and pressure were equipped Valco SS fittings, ferrules and union (details in Table S1).

1.1.2.5 Check-valve

The check-valve inserted between the HPLC pump and the reactor was purchased from IDEX/Upchurch Scientific and was installed in a SS check-valve holder (IDEX/Upchurch Scientific).

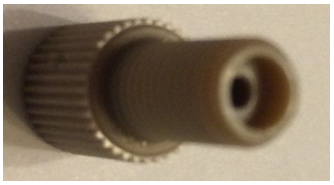
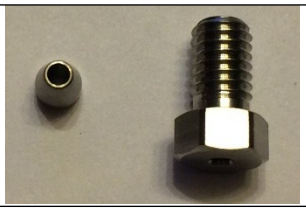
1.1.2.6 Back-pressure regulator

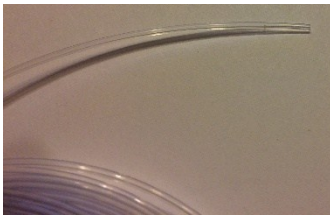
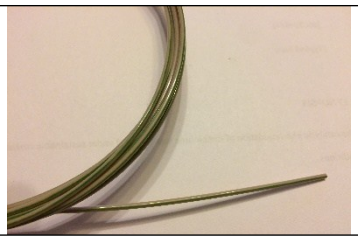
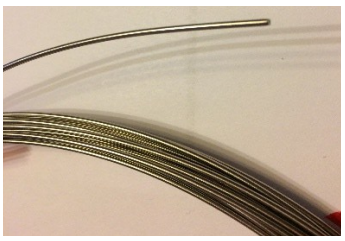
Standard HPLC-type spring-loaded BPRs (IDEX/Upchurch Scientific) set at 250, 500 and 1000 psi were installed in SS BPR holders (IDEX/Upchurch Scientific).

1.1.2.7 Part numbers & vendors

The thermolysis reactor was constructed from standard fluidic elements purchased from IDEX/Upchurch Scientific and Valco Instruments Co. Inc (Table S1).

Table S1. Part numbers and vendors

Part	Details	Vendor	Item#	
Connectors	One-Piece Fingertight Long, PEEK, 10-32 Coned, for 1/16” OD	IDEX/Upchurch Scientific	F-130X	
	Super Flangeless Nuts, natural PEEK 1/4-28 thread for 1/16” OD tubing	IDEX/Upchurch Scientific	P-255X	
	Super Flangeless Ferrule Tefzel (ETFE) and SS ring 1/4-28 thread for 1/16” OD tubing	IDEX/Upchurch Scientific	P-259X	
	SS ZDV union Valco type for 1/16” OD, tubing	IDEX/Upchurch Scientific	U-322	
	SS Nut, standard, for 1/16” OD tubing	VICI (Valco Instruments Co. Inc.)	ZN1-10	

	SS ferrule, 303, for 1/16” OD tubing	VICI (Valco Instruments Co. Inc.)	ZF1-10	
Tubing	High-purity PFA tubing, 1.58 mm outer diameter, 750 µm internal diameter	VICI (Valco Instruments Co. Inc.)	JR-T-4002-M25	
	PEEK tubing (green striped, 1.58 mm outer diameter, 750 µm internal diameter).	VICI (Valco Instruments Co. Inc.)	JR-T-6003-M3	
	316 SS tubing (1.58 mm outer diameter, 500 µm internal diameter)	VICI (Valco Instruments Co. Inc.)	TSS120	
Check-valve	Check Valve Inline Cartridge 1.5 psi	IDEX/Upchurch Scientific	CV-3001	
BPRs	Spring-loaded BPRS with cracking pressure from 250 to 1000 psi	IDEX/Upchurch Scientific	P-788 P-789 P-455	
Cartridge holder	BPR and check-valve cartridge holder, SS	IDEX/Upchurch Scientific	U-469	

1.1.3 Thermoregulated oven

A Thermo Finnigan® (Intersciences) thermoregulated oven was modified to host the thermolysis SS loop. Additional thermocouples and temperature sensors were inserted in the setup.

1.1.4 In-line IR spectrometer

In-line reaction monitoring was carried out with a FlowIR™ (SN# 2964) from Mettler-Toledo equipped with a DTGS detector using HappGenzel apodization, a Silicon probe connected via a FlowIR™ sensor and a high pressure heated 10 µL cell. Sampling was performed from 4000 to 650 cm^{-1} at 8 wavenumber resolution with 128 scans (see also section 2.3).

1.2 Detailed microfluidic setup

The reader is referred to the main manuscript for experimental details (Feed concentrations, flow rates, counter-pressures).

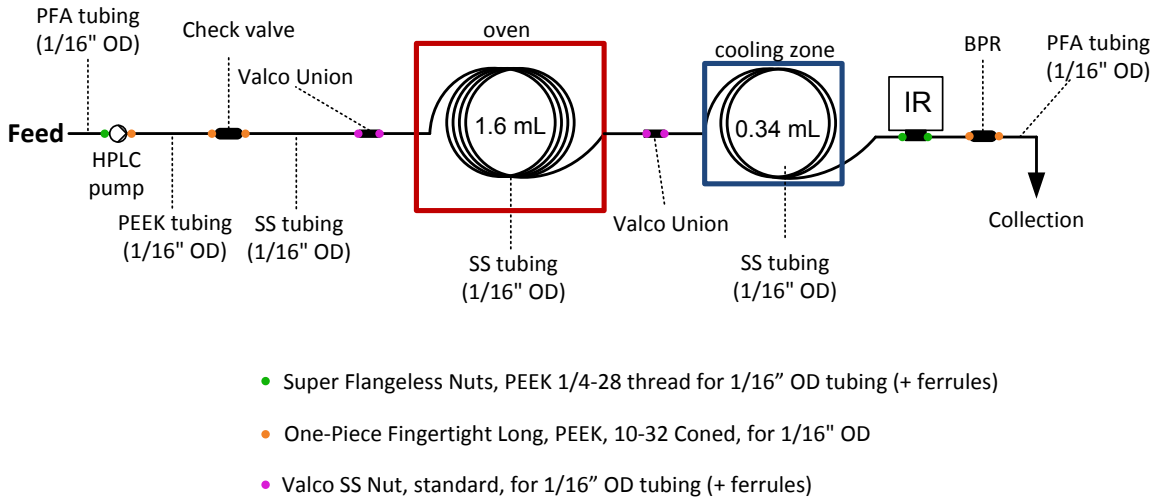


Figure S1. Microfluidic thermolysis setup

1.3 Operation to steady state

The reactor was stabilized for 3 residence times before collection. Steady state was experimentally determined by collecting and analyzing successive fractions.

1.4 Starting up and shutting down procedures

1.4.1 Starting up procedure

The reactor was thoroughly flushed with isopropanol at room temperature for 5 min. Then, the feed was connected to the HPLC pump, and the glycerol dynamic mixture was fed into the reactor at room temperature. The temperature was next set to the desired process temperature, and system was equilibrated for 3 residence times.

1.4.2 Shutting down procedure

The temperature was decreased to room temperature upon pumping of the glycerol mixture. The reactor was next thoroughly flushed with isopropanol at room temperature for 5 min.

1.4.3 In case of clogging

Significant charring was noticed at high temperature (> 340 °C), eventually leading to reactor clogging. The SS coil was removed from the setup and left at 500 °C for 10 hours, and next flushed with water, acetone and isopropanol.

2. Additional experimental details

2.1 Chemicals

Chemicals, suppliers and MSDS are listed in Table S2.

Table S2. Chemicals and suppliers

Product	Supplier	CAS	MSDS
Glycerol, 99%	ABCR	56-81-5	MSDS
Bio-sourced glycerol	Oleon and Mosselman	56-81-5	-
Triethyl orthoformate, 98%	ABCR	122-51-0	MSDS
Formic acid, 97%	ABCR	64-18-6	MSDS
Acetic acid, 99%	ABCR	64-19-7	MSDS
Mesitylene, 99%	ACROS	108-67-8	MSDS
d_6-Acetone > 99%	Euriso-top	666-52-4	MSDS

2.2 Preparation of the feed solutions

2.2.1 Dynamic covalent reactions of glycerol and formic acid

In a typical procedure, the feed solution was prepared by mixing glycerol with 1.5 equiv. of formic acid. No precautions were taken to keep the feed bottle anhydrous, nor was the bottle conditioned under an inert atmosphere. The mixture was instantaneously homogenous. NMR analysis on the feed solution after 15 min indicated the formation of glycerol formate in 32%. The viscosity of the solution (η = 0.016 N s m^{-2}, 22 °C) was significantly reduced by comparison to glycerol (η = 1.09 N s m^{-2}, 22 °C) and could be handled with a standard HPLC pump. Viscosity was measured on a ARES G2 strain-controlled rheometer from TA instruments.

2.2.2 Dynamic covalent reactions of glycerol and triethyl orthoformate

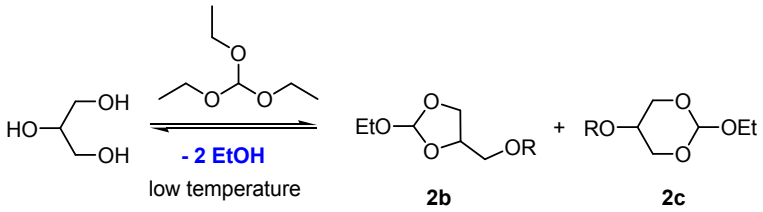
In a typical procedure, the feed solution was prepared by mixing glycerol with 1 equiv. of triethyl orthoformate. No precautions were taken to keep the feed bottle anhydrous, nor was the bottle conditioned under an inert atmosphere. The time required to achieve homogeneity under stirring (500 rpm) depended on the amount of formic acid (Scheme S1, Table S3). Similar trends were observed with acetic acid, leading to a 9:1 **2b**/**2c** mixture (*cis* and *trans* isomers). The viscosity of the solution (η = 0.0038 N s m^{-2}, 22 °C) was significantly reduced and could be handled with a standard HPLC pump. Vacuum distillation of the crude to remove ethanol led to a viscous **2b**/**2c** mixture (η = 0.88 N s m^{-2}, 22 °C). Viscosity was measured on a ARES G2 strain-controlled rheometer from TA instruments.

Table S3. Composition of the dynamic reactive feed solution

Entry	Time (min) for homogeneity	Formic acid (mol%)	NMR yield (combined, %)[a]	Dioxolane **2b** (%)[b]	Dioxane **2c** (%)[b]
1	5	10	94.4	85.0	9.4
2	60	1	93.2	83.2	10
3	180	0.1	92.8	78.8	14

[a] Mesitylene as internal standard (see also section 2.4.3); [b] ^{1}H NMR (400 MHz) ratio obtained by comparing the integration of the signals at 5.84 and 5.25 ppm (**2b** and **2c**, respectively; see references [S1-S8])

The presence of dioxane **2c** was not an issue since it isomerizes towards dioxolane **2b** under acidic conditions at elevated temperature.[S1-S8]



Scheme S1. Dynamic covalent exchange between glycerol and triethyl orthoformate leading to the formation of mixed orthoformates **2b,c**

2.3 In-line IR qualitative analysis

2.3.1 Spectral libraries

Spectral libraries were collected with the iC IR® software (version 4.3) with allyl alcohol (**3a**), allyl formate (**3b**) and feed solutions (see examples in Figures S2-S3). The deoxydehydration reaction can be monitored by following the increase of the characteristic vibration band of **3a** ($\nu_{C=C}$ at 1648 cm^{-1}) and **3b** ($\nu_{C=C}$ at 1656 cm^{-1} and $\nu_{C=O}$ at 1730 cm^{-1}), as well as of CO_2 ($\nu_{C=O}$ at 2340 cm^{-1}) (Figure S3).

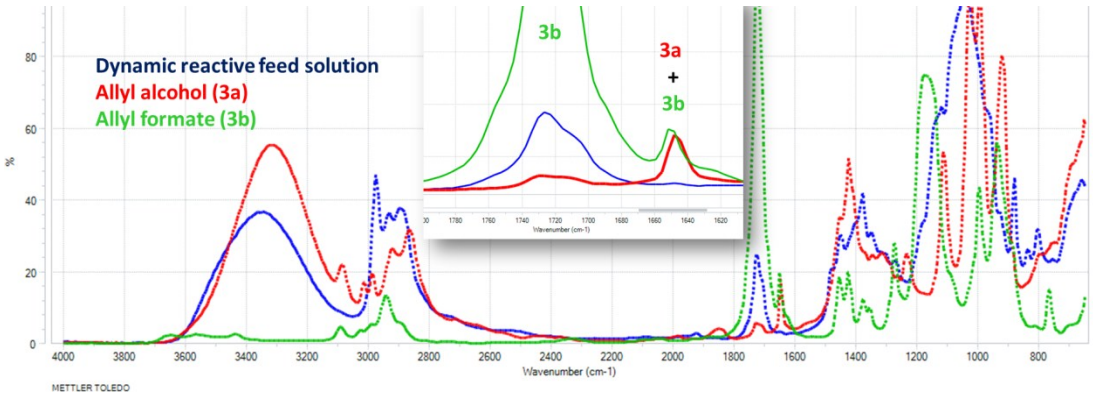
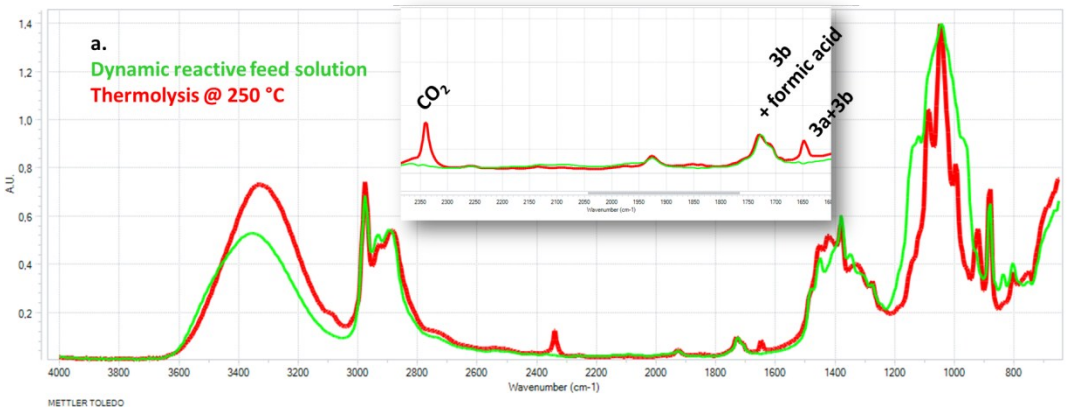


Figure S2. IR spectral library for allyl alcohol (**3a**), allyl formate (**3b**) and a dynamic reactive feed solution (glycerol, 1 equiv. triethyl orthoformate and 10 mol% formic acid)



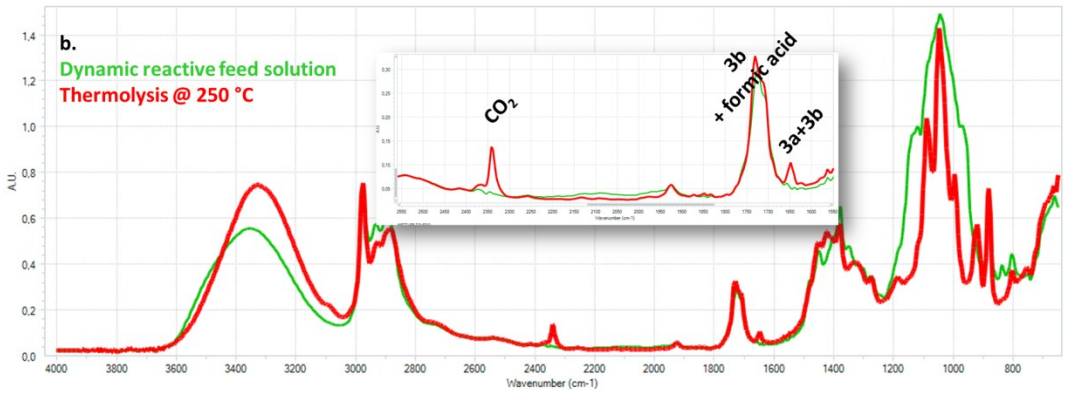


Figure S3. (a) IR spectral library for a dynamic reactive feed solution (glycerol, 1 equiv. triethyl orthoformate and 0.1 mol% formic acid) and the product after thermolysis at 250 °C; (b) IR spectral library for a dynamic reactive feed solution (glycerol, 1 equiv. triethyl orthoformate and 10 mol% formic acid) and the product after thermolysis at 250 °C.

2.3.2 Example

In-line reaction monitoring was recorded with the iC IR® software (version 4.3). Figure S4 illustrates the impact of the temperature on the deoxydehydration reaction. The outcome of the reaction was monitored in real time by following the increase of the characteristic vibration bands of **3a** ($\nu_{C=C}$ at 1648 cm^{-1}) and of CO_2 ($\nu_{C=O}$ at 2340 cm^{-1}). The maximal yield in **3a** was obtained at 250 °C (86%), and then dropped at higher temperatures. The intense signal of CO_2 was already detected at 175 °C (yield of **3a**: 4.2%). The run was stopped at 325 °C.

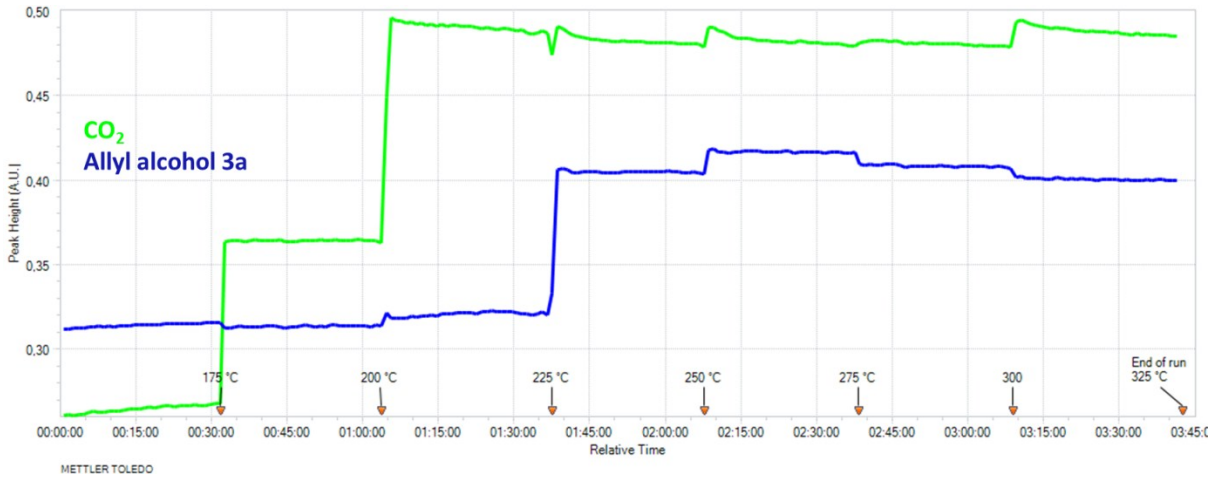


Figure S4. In-line IR monitoring for the deoxydehydration of glycerol in the presence of 1 equiv. of triethyl orthoformate and 10 mol% formic acid at various temperatures

2.4 Off-line NMR quantitative analysis

2.4.1 General procedure

The samples were prepared by adding 600 µL of stock solution of mesitylene (0.04 M) in d_6-acetone to 10 µL of untreated crude reactor effluent. [S9,10] The reactor effluents were collected in closed vials under an inert atmosphere (argon), and kept at 4 °C before analysis. Analytical ^{1}H NMR spectra were recorded at 400 MHz on a Bruker Avance III HD spectrometer (9.4 Tesla) equipped with a high-resolution multinuclear probe that operated in the range of 40-400 MHz. Spectra were recorded in 5 mm NMR tube (Norell). Free induction decays were acquired at 298 K using a standard pulse sequence (Bruker, zg30). The spectral width was 20 ppm (8012.820 Hz). A 30 ° excitation pulse and a 4 s relaxation delay were used to collect 64 scans.

2.4.2 Spectral libraries

Figure S5 regroups ^{1}H NMR spectra (400 MHz, d_6-acetone) of the main reagents and products reported in this study.

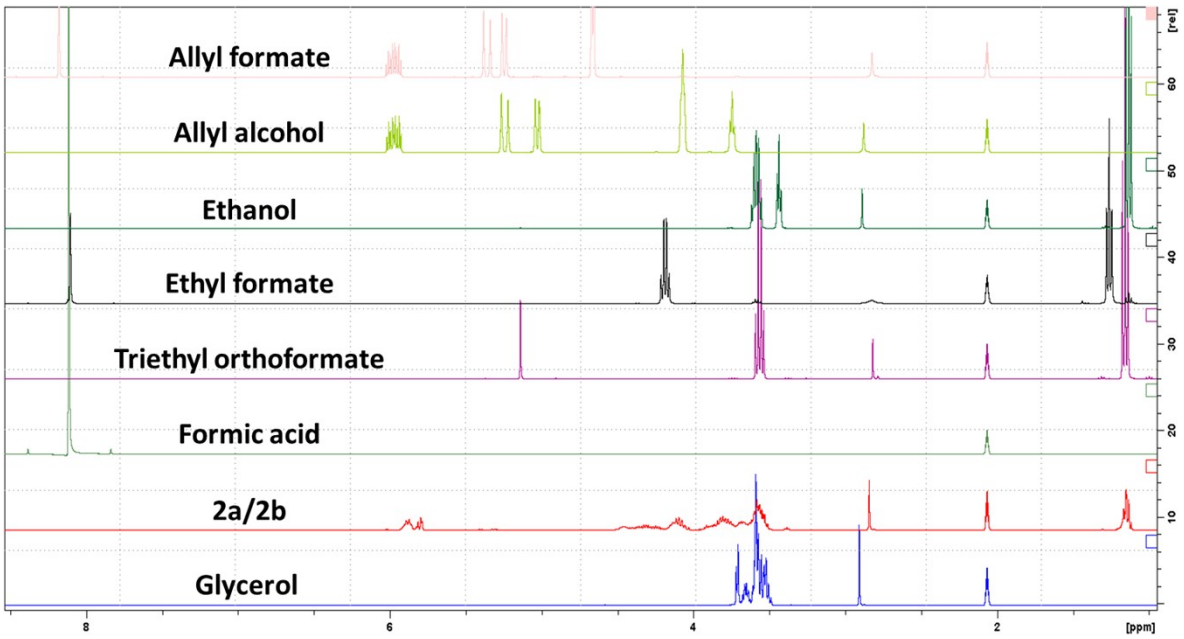


Figure S5. ^{1}H NMR spectral library in d_6-acetone

2.4.3 Determination of NMR yield

Equations S1-3 were utilized for the determination of the NMR yield:

NMR yield for allyl alcohol (**3a**):

$$Y_1(\%) = 100 \times \frac{\left(\frac{3 \times N_{std} \times I_1}{I_{std}}\right)}{N_0} \qquad \text{(Equation S1)}$$

NMR yield for allyl formate (**3b**):

$$Y_2(\%) = 100 \times \frac{\left(\frac{3 \times N_{std} \times I_2}{2 \times I_{std}}\right)}{N_0} \qquad \text{(Equation S2)}$$

$$\text{Combined yield (\%)} = Y_1 + Y_2 \qquad \text{(Equation S3)}$$

N_{std} = amount of internal standard (mesitylene, mol)

I_1 = peak area (integration) of the signal at 5.03 ppm (1H, **3a**)

I_2 = peak area (integration) of the signal at 4.65 ppm (2H, **3b**)

I_{std} = peak area (integration) of the signal at 6.77 ppm (3H, mesitylene)

N_0 = amount of glycerol at t_0 (mol)

The signal at 6.77 ppm (mesitylene internal standard) was selected as reference since it was, for each condition tested, isolated from other interfering signals. The aliphatic signal of mesitylene at 2.5 ppm was less conveniently located, and often interfered with other signals. The relaxation time was increased to 4 s. The signal at 5.03 (ddd, 1H) was selected for the quantification of allyl alcohol (**3a**), since the other olefinic signals at 5.25 and 6.00 ppm overlapped with allyl formate (**3b**). Figure S6 illustrates a typical ^{1}H NMR spectrum for a crude reactor effluent.

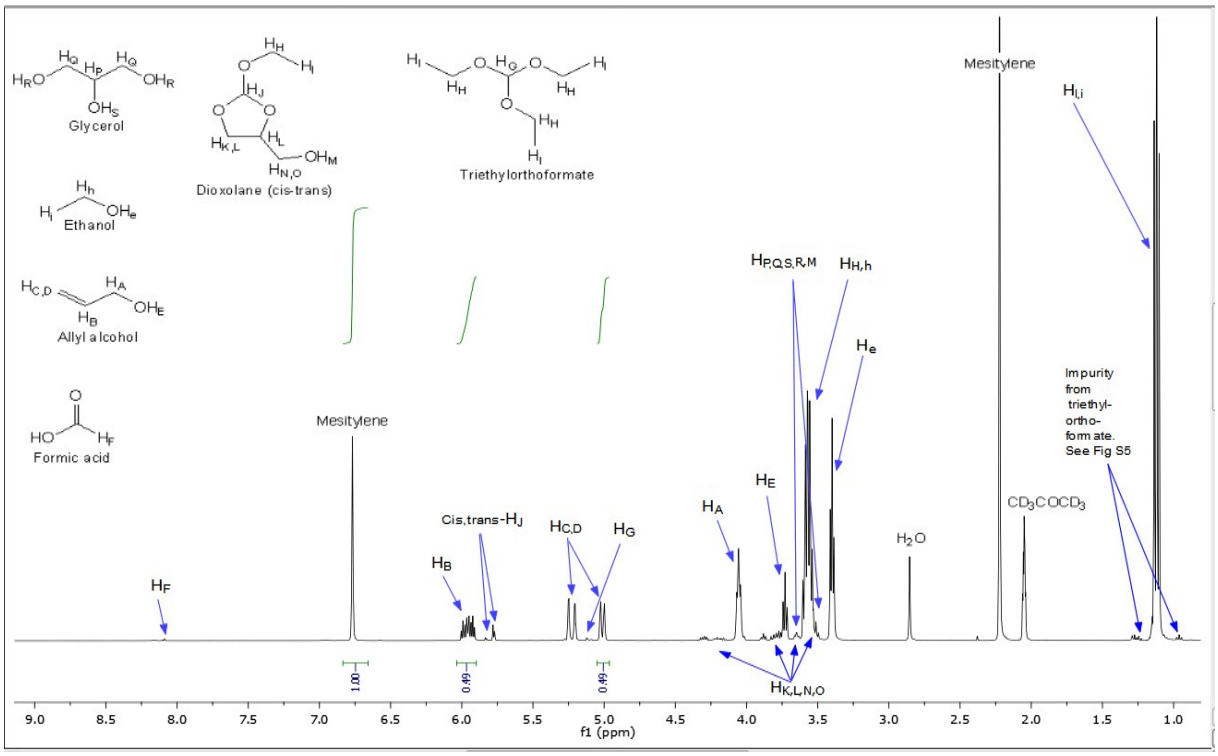


Figure S6.[1]H NMR of a crude reactor effluent: deoxydehydration of glycerol in the presence of triethyl orthoformate (1 equiv.) and formic acid (1 mol%) at 250 °C (6 min residence time, 250 psi) (76% yield for **3a**, see also Table S6, entry 8)

2.4.4 Representative examples

Quantitative off-line analysis was performed via [1]H NMR (400 MHz, d_6-acetone) with mesitylene as an internal standard (see section 2.4.3). Figures S7-S10 illustrate the impact of the temperature, the amount and the nature of the catalyst. The optimum temperature for the deoxydehydration of glycerol in the presence of triethyl orthoformate (1 equiv.) is 250 °C at 250 psi.

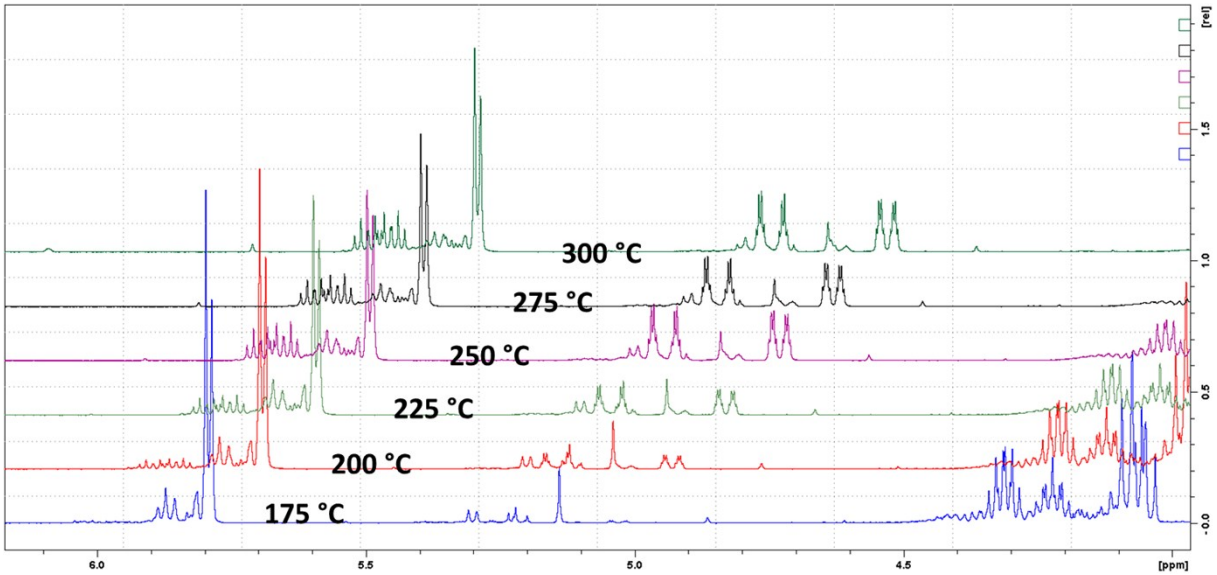


Figure S7. Deoxydehydration of glycerol in the presence of triethyl orthoformate (1 equiv.) at various temperatures (6 min residence time, 250 psi)

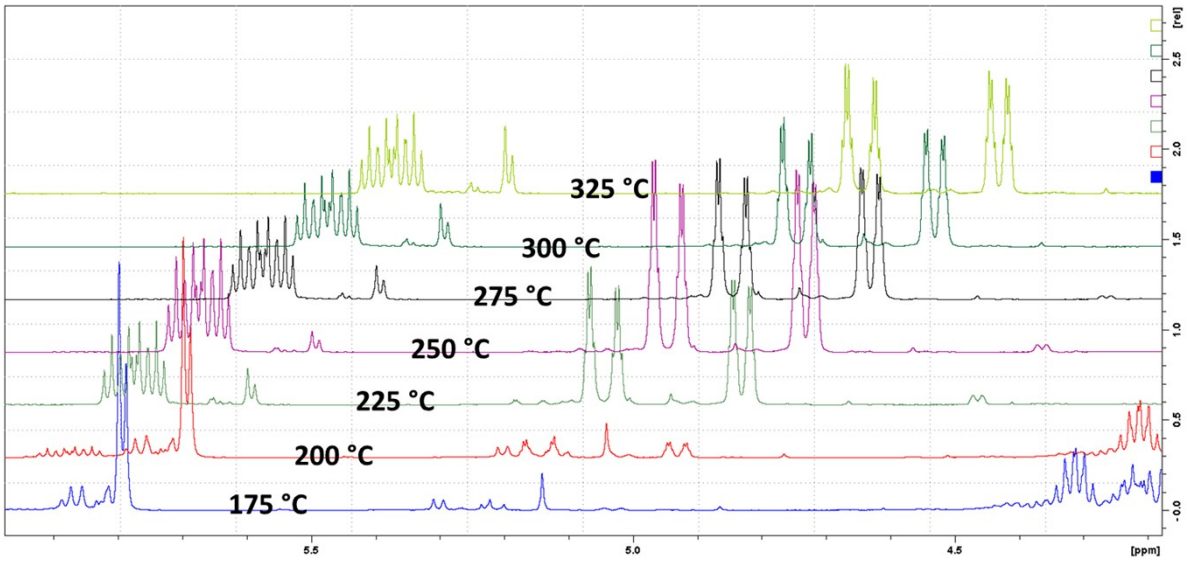


Figure S8. Deoxydehydration of glycerol in the presence of triethyl orthoformate (1 equiv.) and formic acid (10 mol%) at various temperatures (6 min residence time, 250 psi)

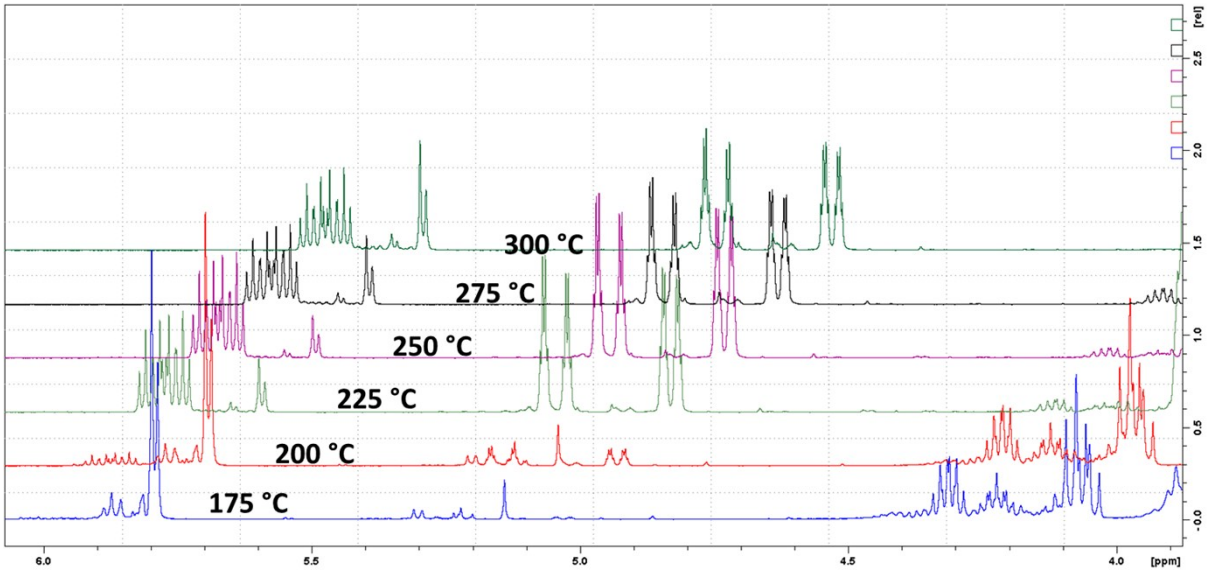


Figure S9. Deoxydehydration of glycerol in the presence of triethyl orthoformate (1 equiv.) and acetic acid (10 mol%) at various temperatures (6 min residence time, 250 psi)

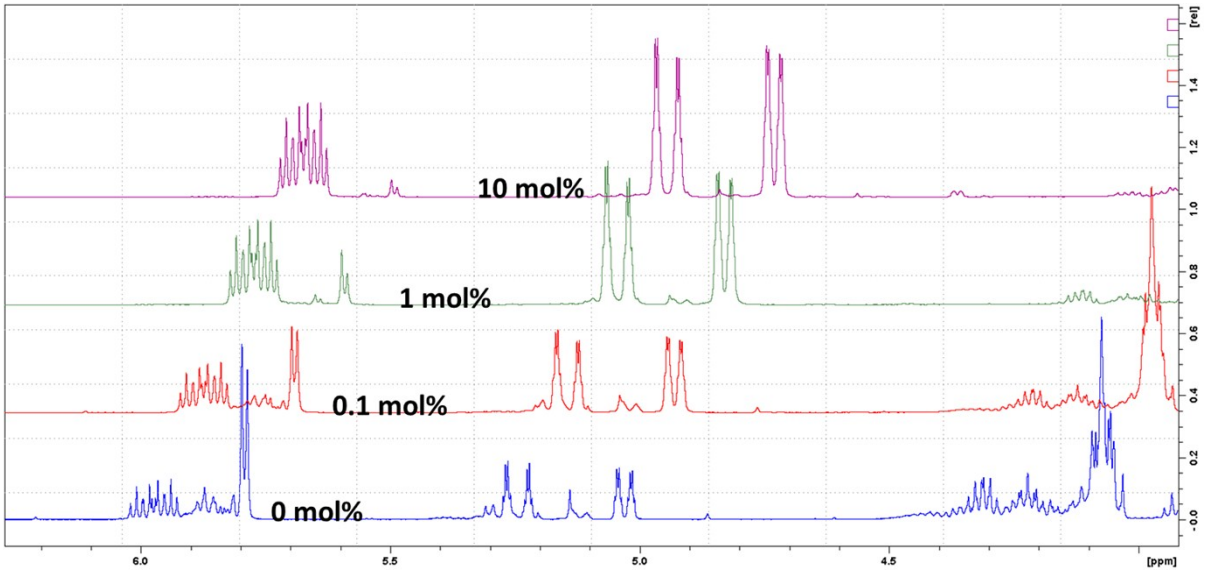


Figure S10. Deoxydehydration of glycerol in the presence of triethyl orthoformate (1 equiv.) at 250 °C with various amounts of formic acid ranging from 0 to 10 mol% (6 min residence time, 250 psi)

2.4.5 Representative runs and results

Table S4. Deoxydehydration of glycerol in the presence of formic acid (1.5 equiv.) (6 min residence time, 1000 psi)

Entry	Temperature	Formic acid (equiv.)	Combined yield (%)	Allyl alcohol (%)	Allyl formate (%)
1	275	1.5	0	0	0
2	300	1.5	11.9	7.3	4.6
3	315	1.5	22.7	13.9	8.8
4	330	1.5	40.4	29.8	10.6
5	345	1.5	45.7	43.9	1.8
6	360	1.5	41.8	40.1	1.7

Table S5. Deoxydehydration of glycerol in the presence of formic acid (2.5 equiv.) and triethyl orthoformate (1-2.5 equiv.) (6 min residence time, 250 psi)

Entry	Temperature	Triethyl orthoformate (equiv.)	Combined yield (%)	Allyl alcohol (%)	Allyl formate (%)
1	300	1	32.7	21.1	11.7
2	315	1	24.9	21.4	3.5
3	330	1	23.5	20.5	3.1
4	345	1	29.6	25.0	4.6
5	360	1	29.6	25.1	4.5
6	300	1.5	50.8	40.2	10.6
7	315	1.5	45.0	39.6	5.4
8	330	1.5	36.5	36.5	0.0
9	345	1.5	33.7	29.3	4.4
10	360	1.5	35.8	31.2	4.6
11	300	2.0	51.8	40.7	11.2
12	315	2.0	52.5	42.1	10.5
13	330	2.0	44.9	37.8	7.2
14	345	2.0	42.9	37.2	5.8
15	360	2.0	41.0	35.7	5.3

16	300	2.5	96.8	76.8	20.0
17	315	2.5	85.1	72.3	12.9
18	330	2.5	83.5	70.1	13.4
19	345	2.5	73.2	59.2	14.0
20	360	2.5	40.6	36.1	4.5

Table S6. Deoxydehydration of glycerol in the presence of triethyl orthoformate (1 equiv.) with formic acid as a catalyst (6 min residence time, 250 psi)

Entry	Temperature	Formic acid (mol%)	Combined yield (%)	Allyl alcohol (%)	Allyl formate (%)
1	175	10	4.2	4.2	0
2	200	10	13.5	12.9	0.6
3	225	10	75.7	73.1	2.7
4	250	10	85.5	83.6	1.9
5	275	10	80.4	79.0	1.4
6	300	10	68.5	67.0	1.5
7	325	10	66.5	64.8	1.7
8	250	1	76.8	76.1	0.7
9	250	0.1	47.7	47.2	0.5
10	175	0	3.9	3.9	/
11	200	0	10.4	10.4	/
12	225	0	16.1	16.1	/
13	250	0	26.1	26.1	/
14	275	0	25.7	25.7	/
15	300	0	27.2	27.2	/

Table S7. Deoxydehydration of glycerol in the presence of triethyl orthoformate (1 equiv.) with acetic acid and a residence of 6 min (250 psi)

Entry	Temperature	Acetic acid (mol%)	Combined yield (%)	Allyl alcohol (%)	Allyl acetate (%)
1	175	10	5.0	5.0	0
2	200	10	13.0	13.0	0

3	225	10	78.5	78.5	0
4	250	10	84.2	84.2	0
5	275	10	76.9	76.9	0
6	300	10	66.1	66.1	0

Table S8. Deoxydehydration of glycerol in the presence of triethyl orthoformate (1 equiv.) in the presence of CO_2 (saturated feed solution) and a residence of 6 min (250 psi)

Entry	Temperature	Added water (mol%)	Combined yield (%)	Allyl alcohol (%)	Allyl formate (%)
1	250	0	51.9	51.0	0.9
2	250	10	44.2	44.2	0.0

2.4.6 Additional runs in other microfluidic setups

In order to exclude any reactor-wall catalytic effects, additional microfluidic setups were constructed from Nickel (1/16" OD x 0.02" ID, ref. TNI120, Valco Instruments Co. Inc.) and Titanium tubing (1/16" OD x 0.02" ID, ref. TTI120, Valco Instruments Co. Inc.). The DODH of glycerol was tested under optimized conditions with a 1:1 glycerol/triethyl orthoformate ratio (Table S9).

Table S9. Deoxydehydration of glycerol in the presence of triethyl orthoformate (1 equiv.) with formic acid and a residence of 6 min (250 psi) in Ni and Ti coils

Entry	Tubing	Formic acid (mol%)	Combined yield (%)	Allyl alcohol (%)	Allyl formate (%)
1	Ni	10	78.6	76.0	2.6
2	Ti	10	84.4	81.4	2.9

2.4.7 Temperature profile in the reactor

The temperature profile can be analytically calculated with by solving the Graetz problem (constant wall temperature). [S11, S12] Figure S11 shows the differences for the theoretical temperature distribution between tubular reactors of 500 and 1000 µm internal diameter (parameters: constant reactor wall; constant residence time; initial temperature: 25 °C; target temperature: 250 °C; thermal conductivity of the reaction mixture: 0.00285 W cm^{-1} K^{-1};

thermal conductivity of the SS tubing: 0.162 W cm^{-1} K^{-1}). It can be seen that for the larger diameter tubing (red curve), the set temperature (250 °C) is reached only after the first quarter of the reactor length, while with the smaller internal diameter tubing (blue curve), the set temperature (250 °C) is attained much faster.

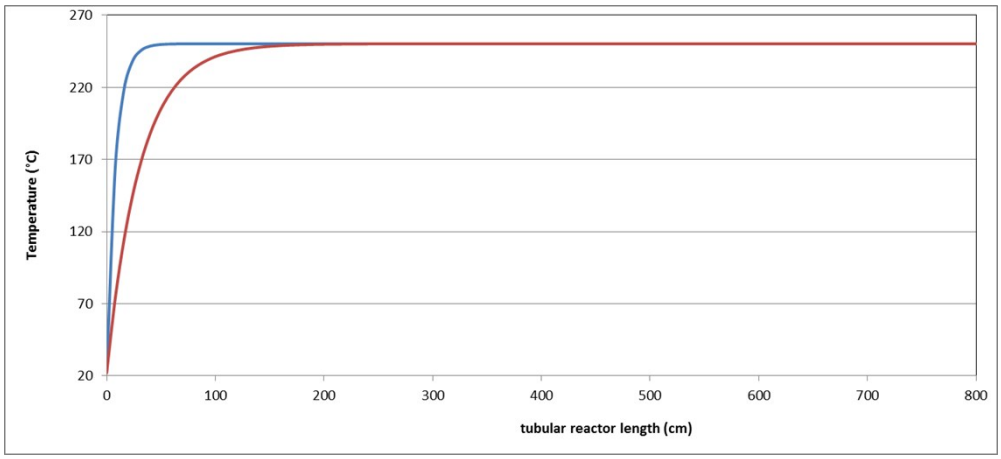


Figure S11. The red and blue curves illustrate the theoretical temperature distribution along the tubular reactor for an internal diameter of 500 and 1000 µm, respectively.

2.4.8 Stability of the feed solution

A large feed solution was prepared (600 mL, 1:1 glycerol/triethyl orthoformate, 10 mol% formic acid) without any precautions and was utilized over 13 days for different runs in a 316SS coil microfluidic setup. The results are illustrated in Figure S12. Consistent results were obtained, with no detectable decrease of the reaction performance.

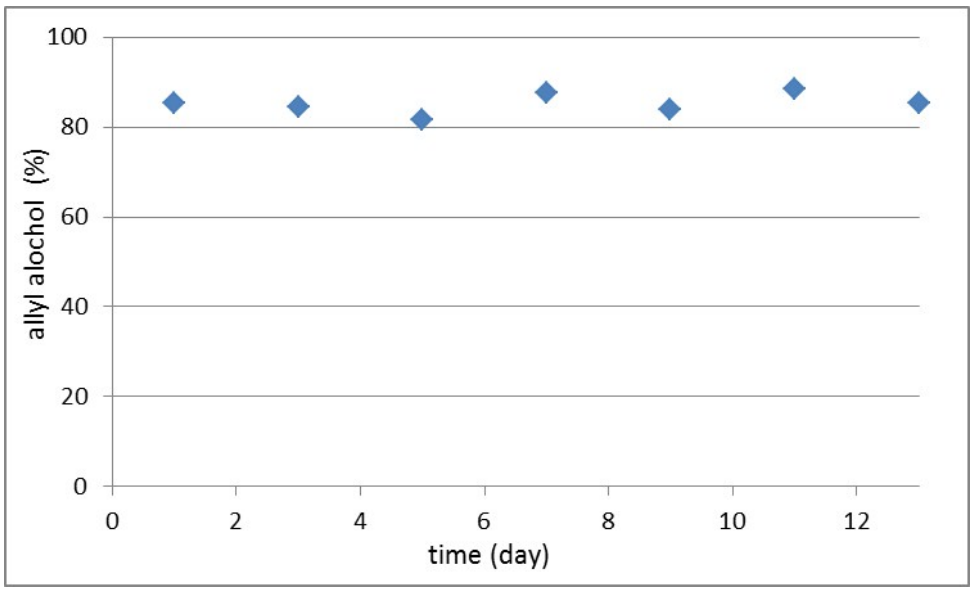


Figure S12. Stability of the feed solution for long runs

2.4.9 Mass balance for some representative examples

The mass balance was evaluated on some representative examples. The feed solution bottle was installed on a precision scale. Samples were collected under optimized conditions (10 mol% formic acid, 1 equiv. triethyl orthoformate, 250 °C, 250 psi) at steady state. For all samples, dissolved CO_2 was removed by sonication (5 min, rt). Table S10 regroups the corresponding data. The values measured are very close to the theoretical values.

Table S10. Mass balance for evaluated on some representative examples

Entry	Glycerol (mmole)	Sample injected for thermolysis (g)	Sample collected after thermolysis[a] (g)	Theoretical mass after thermolysis[b] (g)	ΔM[c] (%)
1	16.47	4.0477	3.2932	3.4241	3.8
2	26.61	6.5386	5.3424	5.5313	3.4
3	27.88	6.8499	5.5873	5.7947	3.6
4	25.35	6.2272	5.0595	5.2679	4.0
5	24.08	5.9158	4.787	5.0045	4.3
6	17.74	4.3590	3.5210	3.6875	4.5

[a] Sonication was applied for 5 min at rt to remove dissolved CO_2; [b] Expected theoretical mass of non-gaseous products (for 86% yield); [c] Deviation between the theoretical mass and the experimental mass

3. Computations

3.1 Thermolysis of allyl formate

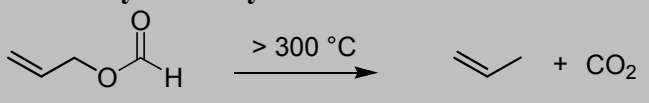
Allyl formate is unstable at high temperature and undergoes CO_2 extrusion to yield propene at temperature above 300 °C. [S13] The rearrangement of allyl formate was studied at the B3LYP/6-31+G** level of theory in gas phase, and using the polarizable continuum model (PCM) for the implicit inclusion of water or ethylene glycol (as a model of glycerol). The extrusion of CO_2 from allyl formate is a strongly exergonic reaction ($\Delta G°$ = -31.5 kcal mol^{-1} in gas phase), and proceeds through a concerted mechanism with a very high activation barrier ($\Delta G^{\neq}$ = 40.4 kcal mol^{-1} in gas phase). The reaction is rather insensitive to medium polarity, with only slight variations of the activation and reaction parameters in water or in ethylene glycol. The results are summarized in Table S11. Cartesian coordinates and absolute energies for all stationary points are listed below (Table S12).

Table S11. Summary of reaction and activation parameters for the thermal rearrangement of allyl formate

kcal mol^{-1}	Activation parameters		Reaction parameters	
	$\Delta H^{\neq}$	$\Delta G^{\neq}$	$\Delta H°$	$\Delta G°$
Gas phase	38.9	40.4	-26.1	-31.5
Water	34.6	36.7	-21.6	-27.2
Ethylene glycol	34.7	36.0	-21.7	-27.8

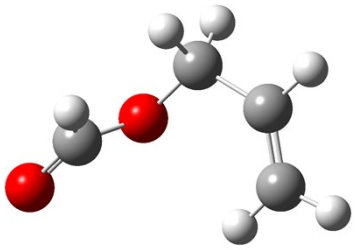
Table S12. Cartesian coordinates and absolute energies for all stationary points are listed below

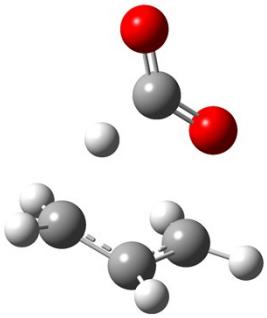
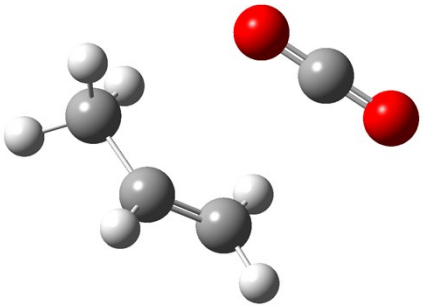
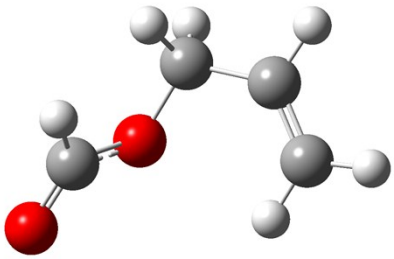
Thermolysis of allyl formate



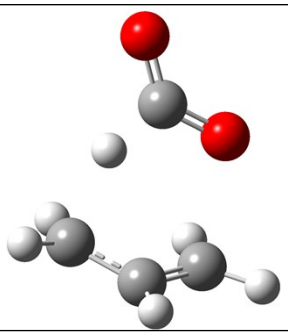
3b

3b (gas phase)				**B3LYP/6-31+G**** (Hartree)
O	0.000000	0.000000	0.000000	H = -306.371472
C	0.000000	0.000000	1.202286	G = -306.410090
O	1.137162	0.000000	1.930784	
C	1.015136	-0.062710	3.360873	
C	1.216958	-1.450544	3.901100	
C	1.480521	-2.537402	3.173380	
H	-0.917510	0.009584	1.819879	
H	1.579617	-2.491597	2.093372	
H	1.614451	-3.505109	3.645976	
H	1.138268	-1.521670	4.985932	
H	0.035306	0.330691	3.669248	

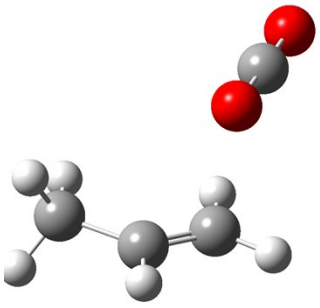


H	1.775388	0.620998	3.753930	
TS (gas phase)				**B3LYP/6-31+G**** (Hartree)
O	-0.009525	0.000000	0.000529	H =-306.309519
C	0.009525	-0.000529	1.220406	G = -306.345717
O	0.875380	0.001058	2.116183	
C	0.086138	-0.213193	4.054273	
C	-1.115797	0.453091	3.918967	
C	-2.047261	-0.094827	3.029642	
H	-1.126729	0.009332	1.751270	
H	0.149405	-1.284323	3.900666	
H	0.941965	0.250101	4.531627	
H	-1.173022	1.509993	4.163665	
H	-2.113872	-1.174690	2.909497	
H	-2.924690	0.465003	2.716630	
Propene + CO_2 (gas phase)				**B3LYP/6-31+G**** (Hartree)
C	0.000000	0.000000	0.000000	H = -306.412996
O	0.744424	0.000000	-0.902104	G = -306.460324
O	-0.740323	-0.016013	0.904689	
C	-1.124468	3.509913	-0.363503	
C	-0.008831	3.599342	-1.095257	
C	0.067586	3.443791	-2.587408	
H	-2.091769	3.312438	-0.821346	
H	-1.111436	3.637251	0.715093	
H	0.934921	3.804261	-0.587730	
H	0.731676	2.614669	-2.861588	
H	0.478666	4.347181	-3.055455	
H	-0.918258	3.251898	-3.022836	
3b (in water)				**B3LYP/6-31+G**** (Hartree)
O	0.000000	0.000000	0.000000	H = -306.382287
C	0.000000	0.000000	1.212029	G = -306.422379
O	1.137425	0.000000	1.917811	
C	1.052369	-0.017292	3.362803	
C	1.483748	-1.333903	3.938615	
C	1.846928	-2.415688	3.245497	
H	-0.916226	0.004811	1.823214	
H	1.862159	-2.423474	2.159896	
H	2.144469	-3.327372	3.753836	
H	1.485057	-1.352738	5.027843	
H	0.029256	0.226585	3.675136	
H	1.702162	0.791472	3.710926	
TS (in water)				**B3LYP/6-31+G**** (Hartree)
O	0.000000	0.000000	0.000000	H = -306.327087
C	0.000000	0.000000	1.238285	G = -306.363927
O	0.897875	0.000000	2.104223	
C	-0.006761	-0.198647	4.224898	
C	-1.177528	0.483800	3.965466	
C	-2.096540	-0.098222	3.097922	
H	-1.081324	0.010217	1.729061	
H	0.071847	-1.264320	4.044698	

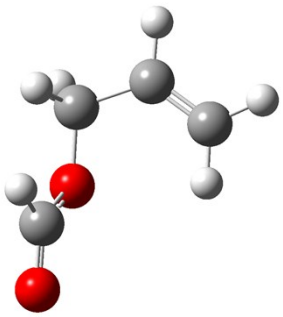
H	0.825180	0.275786	4.733006
H	-1.252493	1.541229	4.200231
H	-2.116727	-1.175643	2.956234
H	-2.949651	0.457831	2.719943



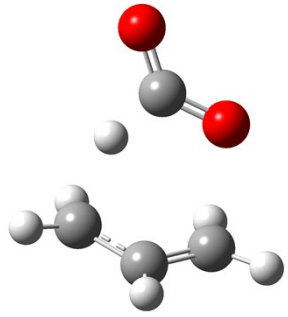
Propene + CO_2 (in water)			**B3LYP/6-31+G**** (Hartree)
C	0.000000	0.000000	0.000000	H = -306.416683
O	1.099795	0.000000	-0.396632	G = -306.465762
O	-1.098700	-0.006240	0.399628	
C	-0.802819	3.487359	-1.153057	
C	-0.110167	3.254075	-2.274080	
C	-0.709380	2.942728	-3.616253	
H	-1.890927	3.464632	-1.140886	
H	-0.305636	3.710559	-0.212932	
H	0.979391	3.289387	-2.233915	
H	-0.358450	1.971405	-3.987034	
H	-0.407362	3.688691	-4.362225	
H	-1.802917	2.920898	-3.574258	



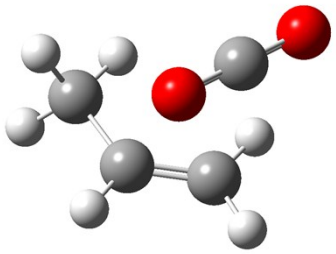
3b (in ethylene glycol)			**B3LYP/6-31+G**** (Hartree)
O	0.000000	0.000000	0.000000	H = -306.382054
C	0.000000	0.000000	1.211783	G = -306.420960
O	1.136964	0.000000	1.919132	
C	1.043481	-0.031727	3.363526	
C	1.350708	-1.388715	3.925581	
C	1.631629	-2.487920	3.221671	
H	-0.916580	0.006629	1.822597	
H	1.665323	-2.483164	2.136454	
H	1.841448	-3.428638	3.720768	
H	1.332918	-1.423301	5.014308	
H	0.046106	0.302777	3.675689	
H	1.763201	0.710396	3.721694	



TS (in ethylene glycol)			**B3LYP/6-31+G**** (Hartree)
O	0.000000	0.000000	0.000000	H = -306.326702
C	0.000000	0.000000	1.237913	G = -306.363526
O	0.897250	0.000000	2.104721	
C	-0.003500	-0.197547	4.219710	
C	-1.175513	0.484451	3.963634	
C	-2.095388	-0.097249	3.096893	
H	-1.081857	0.010384	1.728897	
H	0.074396	-1.263563	4.041283	
H	0.829417	0.277026	4.726040	
H	-1.249754	1.542031	4.198035	
H	-2.116325	-1.174725	2.955606	
H	-2.949148	0.458747	2.720268	



Propene + CO_2 (in ethylene glycol)	**B3LYP/6-31+G**** (Hartree)

C	0.000000	0.000000	0.000000	H = -306.416604
O	1.096997	0.000000	-0.404326	G = -306.465271
O	-1.095840	-0.006378	0.407405	
C	-0.812028	3.485372	-1.149398	
C	-0.115953	3.254152	-2.268697	
C	-0.710886	2.937969	-3.611639	
H	-1.900016	3.457032	-1.139308	
H	-0.317896	3.712582	-0.208632	
H	0.973321	3.295173	-2.226422	
H	-0.353948	1.968175	-3.980695	
H	-0.411621	3.684779	-4.357876	
H	-1.804365	2.910184	-3.571691	

3.2 CO_2 extrusion from dioxolidin-2-ylidene species

The results are summarized in Tables S13-S14. Cartesian coordinates and absolute energies for all stationary points are listed below (Table S15).

Table S13. Activation parameters for the extrusion of CO_2 from dioxolidin-2-ylidene species (kcal mol^{-1}, B3LYP/6-31+G**)

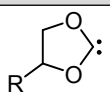
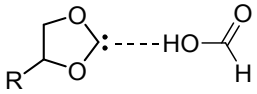
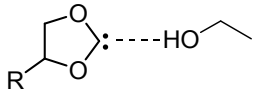
	R	Water (ε = 78.36)		Ethylene glycol (ε = 40.24)	
		$\Delta H^{\neq}$	$\Delta G^{\neq}$	$\Delta H^{\neq}$	$\Delta G^{\neq}$
 **4**	**a** (H)	11.0	10.9	11.0	10.8
	b (CH_2OH)	12.0	11.5	11.9	11.5
	c (CH_2OCOH)	11.4	10.8	11.4	10.8
 **4**·HOCOH	**a** (H)	17.3	15.9	17.2	15.7
	b (CH_2OH)	18.1	16.8	18.0	16.7
	c (CH_2OCOH)	17.4	16.4	17.7	16.6
 **4**·HOEt	**a** (H)	14.1	12.5	14.0	12.6
	b (CH_2OH)	14.9	13.2	14.9	13.2
	c (CH_2OCOH)	14.4	13.1	14.0	12.7

Table S14. Reaction parameters for the extrusion of CO_2 from dioxolidin-2-ylidene species (kcal mol^{-1}, B3LYP/6-31+G**)

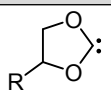
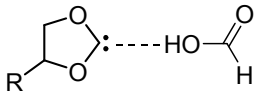
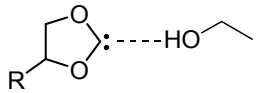
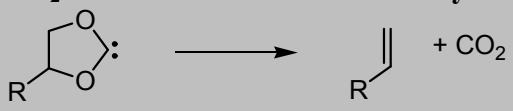
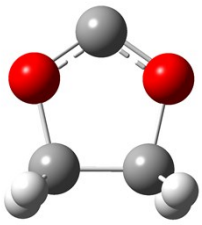
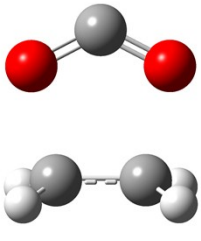
	R	Water (ε = 78.36)		Ethylene glycol (ε = 40.24)	
		$\Delta H°$	$\Delta G°$	$\Delta H°$	$\Delta G°$
 **4**	**a** (H)	-44.5	-52.5	-44.6	-52.6
	b (CH_2OH)	-45.8	-51.1	-45.3	-53.4
	c (CH_2OCOH)	-47.6	-53.0	-47.8	-52.9
 **4**·HOCOH	**a** (H)	-36.4	-48.6	-36.6	-48.9
	b (CH_2OH)	-36.5	-47.6	-37.9	-44.8
	c (CH_2OCOH)	-38.4	-49.3	-38.8	-47.4
 **4**·HOEt	**a** (H)	-40.2	-51.3	-40.4	-50.8
	b (CH_2OH)	-40.3	-50.8	-41.0	-50.8
	c (CH_2OCOH)	-41.8	-52.2	-42.0	-54.0

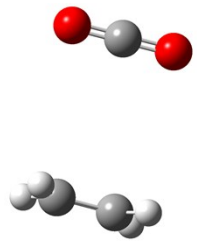
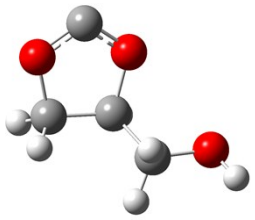
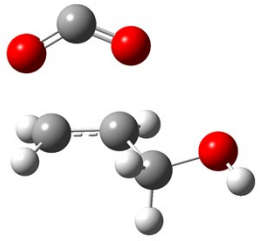
Table S15. Cartesian coordinates and absolute energies for representative stationary points

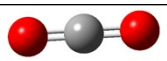
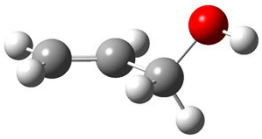
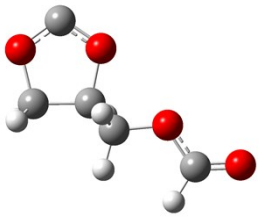
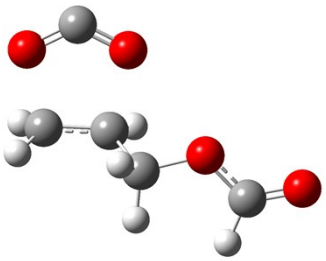
CO_2 extrusion from dioxolidin-2-ylidene species



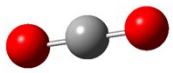
4a (H)
4b (CH_2OH)
4c (CH_2OCOH)

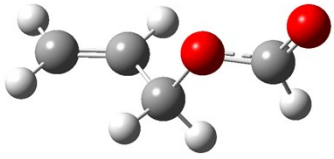
4a (water)				**B3LYP/6-31+G**** (Hartree)
C	0.000000	0.000000	0.000000	H = -267.052022
O	0.000000	0.000000	1.316993	G = -267.084723
C	1.375617	0.000000	1.888860	
C	2.246169	-0.000003	0.644608	
O	1.237226	-0.000001	-0.451550	
H	1.465370	0.896085	2.501266	
H	1.465368	-0.896082	2.501269	
H	2.852169	0.896147	0.518916	
H	2.852165	-0.896155	0.518917	
TS_{4a} (water)				**B3LYP/6-31+G**** (Hartree)
C	0.000000	0.000000	0.000000	H = -267.034428
O	0.000000	0.000000	1.240222	G = -267.067412
C	1.797936	0.000000	1.751175	
C	2.461170	0.000005	0.490344	
O	1.022420	0.000001	-0.702116	
H	1.772398	0.917575	2.328109	
H	1.772401	-0.917579	2.328103	
H	2.922256	0.917660	0.142822	
H	2.922259	-0.917646	0.142816	

ethylene + CO_2 (water)				**B3LYP/6-31+G**** (Hartree)
C	0.000000	0.000000	0.000000	H = -267.122965
O	0.000000	0.000000	1.169113	G = -267.168383
C	3.815977	0.000000	0.658481	
C	3.813857	0.000004	-0.677231	
O	-0.006230	0.000000	-1.169097	
H	3.817323	0.925013	1.229768	
H	3.817319	-0.925016	1.229763	
H	3.813381	0.925020	-1.248516	
H	3.813377	-0.925009	-1.248521	
4b (water)				**B3LYP/6-31+G****
C	0.000000	0.000000	0.000000	H = -381.558066
O	0.000000	0.000000	1.317467	G = -381.597003
C	1.376586	0.000000	1.897593	
C	2.241858	-0.014460	0.645209	
O	1.240513	0.002375	-0.448530	
H	1.456586	0.926424	2.468594	
H	2.867271	0.868541	0.525675	
H	2.834688	-0.922249	0.523010	
C	1.551458	-1.201178	2.804435	
H	2.607520	-1.249342	3.104053	
H	1.305515	-2.118790	2.253679	
O	0.706741	-1.035640	3.940470	
H	0.820103	-1.797369	4.525026	
TS_{4b} (water)				**B3LYP/6-31+G****
C	0.000000	0.000000	0.000000	H = -381.539022
O	0.000000	0.000000	1.237220	G = -381.578632
C	1.843163	0.000000	1.748930	
C	2.459482	0.058599	0.464128	
O	1.022851	0.015673	-0.705362	
H	1.784476	0.921557	2.321031	
H	2.871047	1.005197	0.134217	
H	2.967810	-0.825364	0.091422	
C	1.943179	-1.254251	2.572238	
H	2.980513	-1.345846	2.927179	
H	1.721039	-2.133798	1.953579	
O	1.050894	-1.161682	3.682328	
H	1.240687	-1.890393	4.288581	
Allyl alcohol + CO_2 (water)				**B3LYP/6-31+G****
O	0.000000	0.000000	0.000000	H = -381.631045
C	0.000000	0.000000	1.169128	G = -381.678389
C	5.296093	0.000000	2.435676	
C	5.359696	-0.057492	1.101859	
C	5.726756	1.101284	0.223878	
O	4.673777	1.296687	-0.739497	
O	-0.000533	-0.000078	2.338295	
H	5.490426	0.924364	2.975593	
H	5.056315	-0.875875	3.031776	
H	5.155596	-0.995063	0.584765	

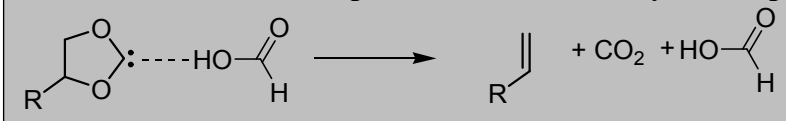
H	6.667930	0.883990	-0.301389	
H	5.872080	2.007624	0.826184	
H	4.984124	1.922670	-1.408244	
4c (water)				**B3LYP/6-31+G****
C	0.000000	0.000000	0.000000	H = -494.885617
O	0.000000	0.000000	1.319867	G = -494.929863
C	1.373245	0.000000	1.896769	
C	2.241136	-0.048119	0.645875	
O	1.239093	-0.013378	-0.446682	
H	1.467711	0.934543	2.451318	
H	2.888078	0.818302	0.522884	
H	2.810680	-0.971319	0.529298	
C	1.533348	-1.195208	2.817512	
H	2.567816	-1.247058	3.173335	
H	1.287166	-2.124436	2.298342	
O	0.626960	-1.078391	3.934477	
C	1.137811	-1.006780	5.174665	
O	0.426348	-0.912953	6.148735	
H	2.237448	-1.042882	5.217219	
TS_{4c} (water)				**B3LYP/6-31+G****
C	0.000000	0.000000	0.000000	H = -494.867422
O	0.000000	0.000000	1.237681	G = -494.912730
C	1.829367	0.000000	1.745869	
C	2.451774	0.030174	0.461410	
O	1.025480	0.006748	-0.701440	
H	1.789651	0.928974	2.306966	
H	2.887583	0.964725	0.128675	
H	2.945669	-0.867128	0.101619	
C	1.920948	-1.250441	2.578486	
H	2.929513	-1.341990	2.999240	
H	1.711008	-2.143456	1.985909	
O	0.955147	-1.216532	3.654335	
C	1.402822	-1.214933	4.918491	
O	0.643327	-1.199283	5.861476	
H	2.499751	-1.229649	5.015015	
Allyl formate + CO_2 (water)				**B3LYP/6-31+G****
O	0.000000	0.000000	0.000000	H = -494.961537
C	0.000000	0.000000	1.169133	G = -495.014360
C	5.398821	0.000000	2.936221	
C	5.648857	-0.154202	1.632934	
C	6.468302	0.809348	0.831600	
O	5.654002	1.366710	-0.248480	

O	-0.000074	-0.000224	2.338301
H	5.766519	0.861559	3.488949
H	4.826511	-0.735327	3.493727
H	5.271208	-1.023572	1.096702
H	7.343868	0.319755	0.390533
H	6.801823	1.656603	1.434226
C	6.042491	1.170500	-1.512637
O	5.415495	1.613282	-2.451863
H	6.966781	0.581226	-1.621083



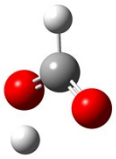


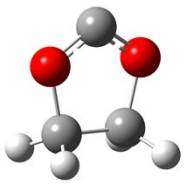
CO_2 extrusion from complexes of dioxolidin-2-ylidene species 4a,c and formic acid



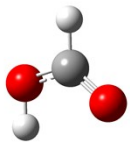
4a•HOCOH (H)
4b•HOCOH (CH_2OH)
4c•HOCOH (CH_2OCOH)

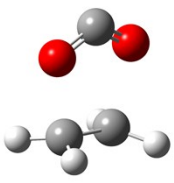
4a·HOCOH (water)			**B3LYP/6-31+G**** (Hartree)
C	0.000000	0.000000	0.000000	H = -456.810379
O	0.000000	0.000000	1.308503	G = -456.857440
C	1.379776	0.000000	1.862422	
C	2.237799	0.000797	0.604696	
O	1.218348	0.000407	-0.477705	
H	1.475938	-0.896818	2.472224	
H	1.475647	0.896097	2.473332	
H	2.840546	0.897677	0.471437	
H	2.841413	-0.895432	0.471064	
H	-1.451307	-0.057875	-0.989007	
O	-2.294988	0.020005	-1.580845	
C	-2.865237	-1.147945	-1.817212	
O	-2.481004	-2.233229	-1.406398	
H	-3.759187	-1.036065	-2.448878	





TS_{4a}·HOCOH (water)			**B3LYP/6-31+G**** (Hartree)
C	0.000000	0.000000	0.000000	H = -456.782850
O	0.000000	0.000000	1.231941	G = -456.832177
C	1.870025	0.000000	1.712813	
C	2.496397	0.000048	0.443047	
O	0.978647	-0.000683	-0.748557	
H	1.831131	-0.920098	2.284467	
H	1.830914	0.920120	2.284402	
H	2.926491	0.920284	0.064772	
H	2.927077	-0.920002	0.064968	
H	-1.866111	0.005179	-0.952107	
O	-2.747803	-0.129102	-1.380820	
C	-3.200546	1.023514	-1.878787	
O	-2.623302	2.091347	-1.818802	
H	-4.178007	0.878619	-2.356977	



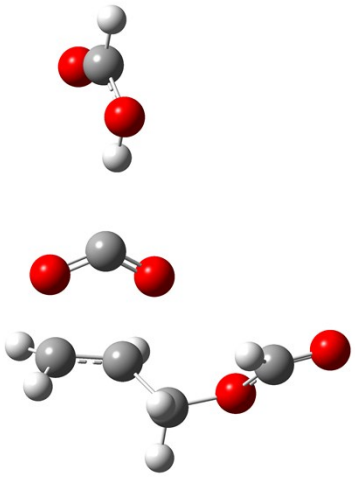


ethylene + CO_2 + HOCOH (water)	**B3LYP/6-31+G**** (Hartree)

H	0.000000	0.000000	0.000000	H = -456.868346
O	0.000000	0.000000	0.977995	G = -456.934904
C	1.258609	0.000000	1.430700	
O	2.251835	0.000364	0.732365	
H	1.271494	-0.000341	2.527589	
O	-0.428511	-0.020748	-2.008382	
C	0.055842	0.091116	-3.068845	
C	-4.682372	0.520935	-4.430362	
C	-4.252118	0.367846	-5.685566	
O	0.531148	0.202632	-4.127867	
H	-3.947318	1.216812	-6.292542	
H	-4.987300	-0.328033	-3.823442	
H	-4.745402	1.500823	-3.963534	
H	-4.189289	-0.612032	-6.152433	
4b·HOCOH (water)				**B3LYP/6-31+G**** (Hartree)
C	0.000000	0.000000	0.000000	H = -571.316461
O	0.000000	0.000000	1.312400	G = -571.370017
C	1.378685	0.000000	1.872226	
C	2.234795	0.020978	0.608429	
O	1.220324	0.014186	-0.471062	
H	1.461153	0.910152	2.466544	
H	2.826278	0.926641	0.489872	
H	2.854932	-0.864912	0.469238	
H	-1.463828	0.031530	-1.009712	
O	-2.331466	-0.060881	-1.553854	
C	-2.609853	1.022117	-2.259356	
O	-1.944898	2.046381	-2.297105	
H	-3.541256	0.896655	-2.831083	
C	1.561015	-1.231508	2.741845	
H	2.588761	-1.269887	3.109874	
H	1.349922	-2.146524	2.179702	
O	0.717185	-1.142069	3.892867	
H	1.028997	-1.750434	4.566858	
TS$_{4b}$·HOCOH (water)				**B3LYP/6-31+G**** (Hartree)
C	0.000000	0.000000	0.000000	H = -571.287662
O	0.000000	0.000000	1.229160	G = -571.343192
C	1.924338	0.000000	1.706049	
C	2.495464	0.062778	0.410137	
O	0.978847	0.014054	-0.752148	
H	1.847714	0.922285	2.274422	
H	2.868421	1.014237	0.050705	
H	2.976556	-0.820779	0.002850	
H	-1.845622	-0.021409	-0.967088	
O	-2.723772	-0.162773	-1.402682	
C	-3.181157	0.985030	-1.906767	
O	-2.612568	2.057547	-1.845243	
H	-4.153926	0.831907	-2.392052	
C	2.022492	-1.255635	2.524108	
H	3.066151	-1.356266	2.858712	
H	1.782845	-2.133013	1.909038	

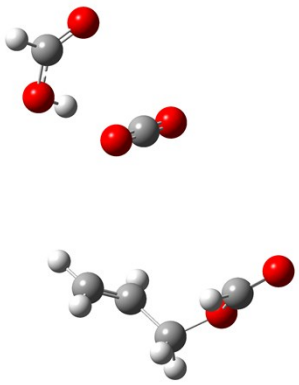
O	1.152740	-1.154099	3.649647	
H	1.350683	-1.880663	4.255916	
Allyl alcohol + CO_2 + HOCOH (water)				**B3LYP/6-31+G**** (Hartree)
H	0.000000	0.000000	0.000000	H = -571.374685
O	0.000000	0.000000	0.978042	G = -571.445937
C	1.258416	0.000000	1.431283	
O	2.252067	0.001240	0.733566	
H	1.270733	-0.001143	2.528188	
O	-0.408973	-0.057898	-2.009891	
C	-0.014617	0.319749	-3.046090	
C	-4.267429	0.556659	-3.843445	
C	-4.006128	0.182272	-5.099721	
O	0.373201	0.692484	-4.080718	
C	-4.308125	-1.177677	-5.654197	
H	-4.715654	-1.829115	-4.870019	
H	-5.058134	-1.092981	-6.453741	
H	-3.562200	0.889781	-5.799978	
H	-4.706291	-0.131612	-3.124090	
H	-4.060153	1.564639	-3.495562	
O	-3.092919	-1.732829	-6.192979	
H	-3.318135	-2.523639	-6.702300	
4c·HOCOH (water)				**B3LYP/6-31+G**** (Hartree)
C	0.000000	0.000000	0.000000	H = -684.64365
O	0.000000	0.000000	1.312400	G = -684.702609
C	1.378686	0.000000	1.872222	
C	2.234800	0.020977	0.608428	
O	1.220323	0.014195	-0.471063	
H	1.461149	0.910151	2.466543	
H	2.826280	0.926643	0.489877	
H	2.854937	-0.864915	0.469249	
H	-1.463838	0.031530	-1.009698	
O	-2.331463	-0.060868	-1.553859	
C	-2.609855	1.022141	-2.259343	
O	-1.944905	2.046409	-2.297076	
H	-3.541255	0.896682	-2.831074	
C	1.561013	-1.231504	2.741847	
H	2.588761	-1.269884	3.109872	
H	1.349911	-2.146520	2.179708	
O	0.710600	-1.141359	3.901870	
C	-0.356744	-1.955514	3.983978	
O	-1.120088	-1.902449	4.920606	
H	-0.459247	-2.659807	3.144392	
TS_{4c}·HOCOH (water)				**B3LYP/6-31+G**** (Hartree)
C	0.000000	0.000000	0.000000	H = -684.615981
O	0.000000	0.000000	1.230900	G = -684.676508
C	1.900079	0.000000	1.709972	
C	2.488746	0.038063	0.419427	
O	0.983374	0.008867	-0.744526	
H	1.841534	0.927840	2.270592	
H	2.885481	0.979586	0.059452	

H	2.958480	-0.857139	0.024891
H	-1.867136	-0.011891	-0.980690
O	-2.742199	-0.150803	-1.419402
C	-3.195717	1.001436	-1.918439
O	-2.624645	2.071755	-1.847791
H	-4.166832	0.852789	-2.408132
C	1.976531	-1.252875	2.540622
H	2.978490	-1.349470	2.969193
H	1.767879	-2.147396	1.946123
O	1.079635	-1.172358	3.670445
C	-0.034313	-1.921158	3.656676
O	-0.842775	-1.870161	4.556320
H	-0.132555	-2.577194	2.778851

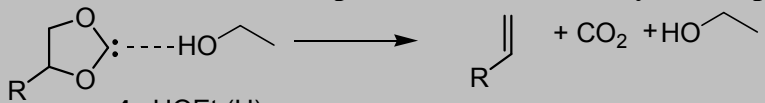


Allyl formate + CO_2 + HOCOH (water)			**B3LYP/6-31+G**** (Hartree)
H	0.000000	0.000000	0.000000
O	0.000000	0.000000	0.978027
C	1.258515	0.000000	1.431119
O	2.252012	0.001462	0.733213
H	1.270987	-0.001367	2.528019
O	-0.416713	-0.073256	-2.007864
C	-0.043375	0.316536	-3.047353
C	-4.442563	0.238635	-3.653882
C	-4.316197	0.058194	-4.971890
O	0.322967	0.701085	-4.085468
C	-4.659683	-1.223642	-5.668171
O	-3.518395	-1.711736	-6.446765
C	-2.709071	-2.607467	-5.872208
O	-1.716215	-3.024843	-6.430631
H	-3.025503	-2.935071	-4.869521
H	-4.978603	-1.996646	-4.962842
H	-5.444999	-1.081461	-6.413899
H	-3.969241	0.869479	-5.609820
H	-4.787444	-0.557909	-2.998485
H	-4.213399	1.193042	-3.189307

H = -684.704779
G = -684.781156



CO_2 extrusion from complexes of dioxolidin-2-ylidene species 4a,c and ethanol

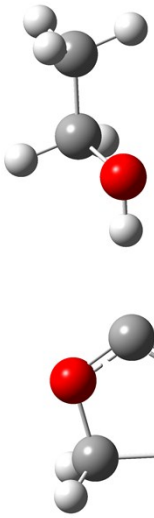


4a•HOEt (H)
4b•HOEt (CH_2OH)
4c•HOEt (CH_2OCOH)

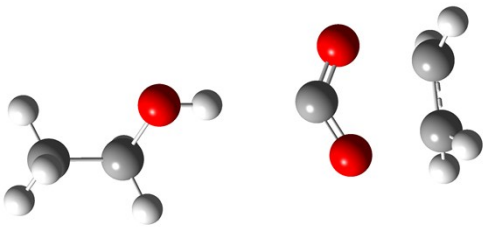
4a·HOEt (water)			**B3LYP/6-31+G**** (Hartree)
C	0.000000	0.000000	0.000000
O	0.000000	0.000000	1.312630
C	1.377489	0.000000	1.875528
C	2.241897	-0.002398	0.624504
O	1.227869	-0.000979	-0.464620
H	1.469916	-0.895308	2.488391

H = -422.036978
G = -422.087657

H	1.470921	0.897110	2.485623
H	2.848361	0.892628	0.494494
H	2.844781	-0.899998	0.495468
H	-1.635873	0.003269	-1.131712
O	-2.450638	-0.000222	-1.689960
C	-2.386521	1.097837	-2.602789
H	-1.498586	1.007364	-3.246671
H	-2.298574	2.046792	-2.052552
C	-3.644828	1.110635	-3.456946
H	-4.537497	1.222793	-2.831925
H	-3.615693	1.944489	-4.166645
H	-3.737599	0.179008	-4.025708

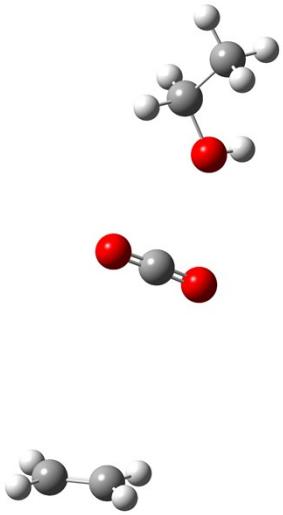


TS_{4a}·HOEt (water)			**B3LYP/6-31+G**** (Hartree)
C	0.000000	0.000000	0.000000	H = -422.014522
O	0.000000	0.000000	1.234986	G = -422.067704
C	1.841653	0.000000	1.727856	
C	2.482455	0.001504	0.461555	
O	0.995514	0.001127	-0.730967	
H	1.808067	-0.919776	2.300531	
H	1.807593	0.918545	2.302471	
H	2.924274	0.921329	0.095753	
H	2.925416	-0.917128	0.094143	
H	-1.998728	-0.066618	-0.973725	
O	-2.877530	-0.136597	-1.387872	
C	-3.026534	0.929878	-2.337581	
H	-2.235138	0.870357	-3.097738	
H	-2.933620	1.900835	-1.831179	
C	-4.392565	0.807606	-2.991505	
H	-5.189385	0.876766	-2.243340	
H	-4.535623	1.612046	-3.720651	
H	-4.489813	-0.150260	-3.513481	

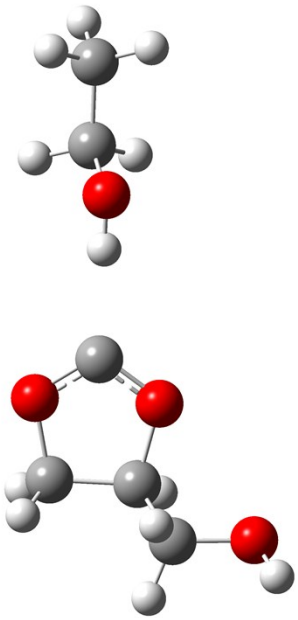


ethylene + CO_2 + HOEt (water)			**B3LYP/6-31+G**** (Hartree)
C	0.000000	0.000000	0.000000	H = -422.101103
O	0.000000	0.000000	1.169294	G = -422.169436
C	5.087536	0.000000	1.369020	
C	5.590199	0.652678	0.317653	
O	0.043265	-0.005332	-1.168400	
H	5.051513	-1.086104	1.403315	
H	4.693777	0.527762	2.234178	
H	5.626239	1.738764	0.283380	
H	5.983986	0.124865	-0.547445	
H	-3.195157	0.576324	0.867652	
O	-2.840300	0.266166	0.022713	
C	-3.778472	0.595067	-1.016472	
H	-3.302387	0.265683	-1.944351	
H	-3.904562	1.684746	-1.073486	

C	-5.127050	-0.089657	-0.831648
H	-5.610266	0.236390	0.096741
H	-5.795249	0.160954	-1.663377
H	-5.010459	-1.177857	-0.797896

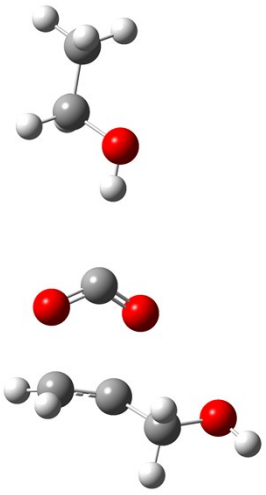


4b·HOEt (water)			**B3LYP/6-31+G**** (Hartree)
C	0.000000	0.000000	0.000000	H = -536.543049
O	0.000000	0.000000	1.312804	G = -536.599475
C	1.379869	0.000000	1.883830	
C	2.238019	-0.015505	0.624323	
O	1.230692	0.002992	-0.462252	
H	1.462276	0.927400	2.452577	
H	2.863199	0.866886	0.500532	
H	2.828082	-0.924241	0.497300	
H	-1.629040	-0.040866	-1.141258	
O	-2.436378	-0.083914	-1.708512	
C	-2.705050	1.219979	-2.228518	
H	-1.845369	1.582708	-2.812011	
H	-2.868819	1.932728	-1.406113	
C	-3.940902	1.158554	-3.112862	
H	-4.810911	0.817535	-2.541152	
H	-4.166491	2.148864	-3.523019	
H	-3.786001	0.467767	-3.948857	
C	1.559351	-1.200184	2.790760	
H	2.618036	-1.248437	3.080993	
H	1.308143	-2.118369	2.243459	
O	0.723865	-1.029760	3.931954	
H	0.836391	-1.792089	4.515945	

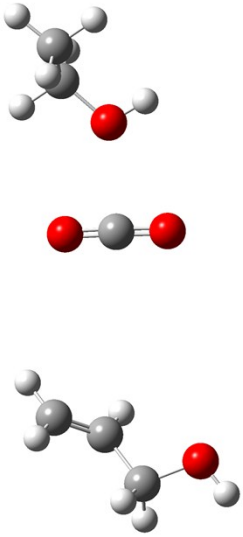


TS$_{4b}$·HOEt (water)			**B3LYP/6-31+G**** (Hartree)
C	0.000000	0.000000	0.000000	H = -536.519254
O	0.000000	0.000000	1.232109	G = -536.5785080
C	1.892185	0.000000	1.722977	
C	2.481025	0.062727	0.431370	
O	0.995936	0.016462	-0.734302	
H	1.822459	0.921407	2.293793	
H	2.868943	1.012864	0.084128	
H	2.973203	-0.820436	0.036381	
H	-1.976645	-0.098302	-0.995995	
O	-2.849249	-0.181151	-1.421634	

C	-2.988534	0.863693	-2.396292
H	-2.184542	0.792594	-3.142153
H	-2.909237	1.845925	-1.909640
C	-4.342980	0.719455	-3.069598
H	-5.152380	0.801144	-2.336356
H	-4.478075	1.506405	-3.819077
H	-4.426701	-0.250529	-3.571169
C	1.990942	-1.256120	2.541541
H	3.032267	-1.353891	2.883697
H	1.757736	-2.133585	1.924082
O	1.112718	-1.159039	3.661439
H	1.306913	-1.887625	4.266481

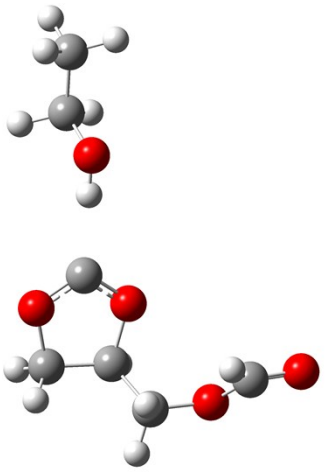


Allyl alcohol + CO_2 + HOEt (water)			**B3LYP/6-31+G**** (Hartree)
C	0.000000	0.000000	0.000000	H = -536.607245
O	0.000000	0.000000	1.169323	G = -536.680459
C	5.607572	0.000000	-0.555260	
C	4.919711	-0.284003	-1.665521	
O	0.044687	-0.005231	-1.168354	
H	5.734427	1.035889	-0.240821	
H	4.487009	0.498725	-2.282043	
H	4.774585	-1.309451	-1.998928	
H	-3.254753	0.500702	0.807919	
O	-2.832168	0.277809	-0.033300	
C	-3.643038	0.794099	-1.102830	
H	-3.089912	0.561619	-2.017206	
H	-3.713016	1.887383	-1.023029	
C	-5.033279	0.171688	-1.142210	
H	-5.593301	0.399992	-0.227733	
H	-5.601146	0.568999	-1.991190	
H	-4.970569	-0.916375	-1.247453	
C	6.265092	-1.027629	0.316411	
H	7.354863	-0.882645	0.301967	
H	6.048965	-2.038617	-0.053050	
O	5.777283	-0.865263	1.662151	
H	6.324125	-1.402009	2.252358	

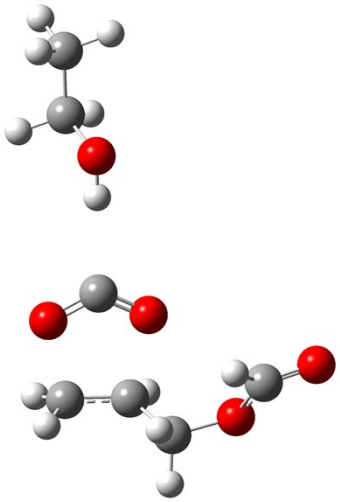


4c·HOEt (water)			**B3LYP/6-31+G**** (Hartree)
C	0.000000	0.000000	0.000000	H = -649.870685
O	0.000000	0.000000	1.316516	G = -649.932148
C	1.375698	0.000000	1.884682	
C	2.238439	0.022061	0.627620	
O	1.229373	0.015343	-0.458422	
H	1.455702	0.908864	2.481529	
H	2.831045	0.927707	0.513563	
H	2.860247	-0.863446	0.492202	
H	-1.640385	-0.051883	-1.144599	
O	-2.447294	-0.098748	-1.709883	
C	-2.722375	1.204342	-2.229779	

H	-1.865123	1.570199	-2.814700
H	-2.887741	1.916159	-1.407026
C	-3.959397	1.136927	-3.111843
H	-4.826948	0.792518	-2.538469
H	-4.189848	2.126088	-3.521998
H	-3.802907	0.446493	-3.947814
C	1.552842	-1.232798	2.753575
H	2.576546	-1.271550	3.132445
H	1.347707	-2.146856	2.187715
O	0.691668	-1.148061	3.906992
C	-0.384275	-1.951769	3.967750
O	-1.159262	-1.900385	4.895232
H	-0.482834	-2.647333	3.120482

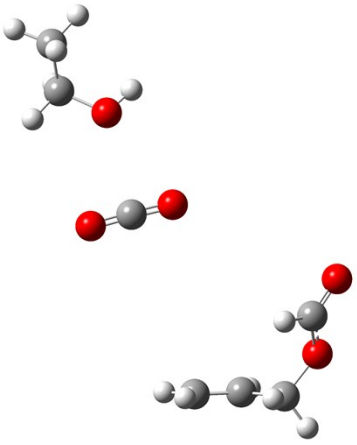


TS_{4c}·HOEt (water)			**B3LYP/6-31+G**** (Hartree)
C	0.000000	0.000000	0.000000	H = -649.847781
O	0.000000	0.000000	1.233755	G = -649.911324
C	1.871467	0.000000	1.725135	
C	2.475354	0.034970	0.437990	
O	0.999699	0.009830	-0.727437	
H	1.820154	0.928056	2.286239	
H	2.887915	0.973789	0.088594	
H	2.953650	-0.861298	0.056056	
H	-1.977830	-0.076449	-1.047195	
O	-2.831370	-0.142505	-1.510732	
C	-3.100650	1.109350	-2.160923	
H	-2.291511	1.349616	-2.864592	
H	-3.150332	1.916826	-1.417120	
C	-4.422776	0.994919	-2.900699	
H	-5.238766	0.768362	-2.206275	
H	-4.654798	1.937843	-3.406917	
H	-4.379152	0.201866	-3.654743	
C	1.947266	-1.251383	2.558939	
H	2.946220	-1.345617	2.994534	
H	1.743457	-2.147283	1.964766	
O	1.043284	-1.171659	3.683800	
C	-0.077479	-1.909450	3.655873	
O	-0.892854	-1.856863	4.549346	
H	-0.174788	-2.558585	2.772917	



Allyl formate + CO_2 + HOEt (water)			**B3LYP/6-31+G**** (Hartree)
C	0.000000	0.000000	0.000000	H = -649.93735
O	0.000000	0.000000	1.169310	G = -650.015313
C	5.432306	0.000000	1.940349	
C	5.163339	-0.157083	0.640931	
O	0.045507	-0.005419	-1.168343	
H	5.522427	0.996899	2.368839	
H	5.037317	0.697509	-0.017139	
H	5.069602	-1.142825	0.190881	
H	-3.252278	0.499804	0.807507	
O	-2.830079	0.277994	-0.034193	

C	-3.641902	0.794736	-1.102782
H	-3.089074	0.563583	-2.017678
H	-3.712671	1.887884	-1.021847
C	-5.031692	0.171318	-1.142040
H	-5.591386	0.398305	-0.227038
H	-5.600308	0.569044	-1.990322
H	-4.968228	-0.916595	-1.248377
C	5.656893	-1.141649	2.884903
H	6.653549	-1.107771	3.330699
H	5.522931	-2.109866	2.393489
O	4.752439	-1.046224	4.033603
C	3.612413	-1.743396	3.990355
O	2.790058	-1.682392	4.880184
H	3.494732	-2.375032	3.096050



4. References

[S1] G. Crank and F. W. Eastwood, *Aust. J. Chem.*, 1964, **17**, 1385–1391.

[S2] G. Crank and F. W. Eastwood, *Aust. J. Chem.*, 1964, **17**, 1392–1398.

[S3] Y. Yokoyama, A. Buyle Padias, F. De Blauwe and H. K. Hall, *Macromolecules*, 1980, **13**, 252–261.

[S4] H. R. Allcock and S. Kwon, *Macromolecules*, 1988, **21**, 1980–1985.

[S5] B. M. Smith, T. M. Kubczyk and A. E. Graham, *RSC Adv.*, 2012, **2**, 2702–2706.

[S6] B. Wang, Y. Shen, J. Sun, F. Xu and R. Sun, *RSC Adv.*, 2014, **4**, 18917–18923

[S7] M. J. Climent, A. Corma and S. Iborra, *Green Chem.*, 2014, **16**, 516–547.

[S8] R.-C. Brachvogel and M. von Delius, *Chem. Sci.*, 2015, **6**, 1399–1403.

[S9] A. Axelsson, A. Antoine-Michard and H. Sundén, *Green Chem.*, 2017, doi 10.1039/C7GC00471K.

[S10] M. Shiramizu and F. D. Toste, *Angew. Chem. Int. Ed.*, 2012, **51**, 8082–8086.

[S11] A. Adamo, R. L. Beingessner, M. Behnam, J. Chen, T. F. Jamison, K. F. Jensen, J.-C. M. Monbaliu, A. S. Myerson, E. M. Revalor, D. R. Snead, T. Stelzer, N. Weeranoppanant, S. Y. Wo and P. Zhang, *Science*, 2016, **352**, 61–67.

[S12] W. M. Deen, *Analysis of Transport Phenomena,* Oxford Univ. Press, Ed. 2, 2012.

[S13] J. M. Vernon and D. J. Waddington, *J. Chem. Soc. D,* 1969, 623–624.