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Investigations on heterogeneously catalysed condensations of glycerol to cyclic acetals

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Dedicated to Prof. Bernhard Lücke on the occasion of his 70th birthday

Abstract

The acid-catalysed condensation of glycerol, a chemical from renewable materials, with benzaldehyde, formaldehyde, acetone (acetalisation), and their dimethyl acetals (transacetalisation) to mixtures of [1,3]dioxan-5-ols and [1,3]dioxolan-4-yl-methanols was investigated. Various solid acids were evaluated as heterogeneous catalysts for the desired glycerol conversion into these potential novel platform chemicals. [1,3]dioxan-5-ols are of particular interest as precursors for 1,3-propanediol derivatives. Therefore, the reported investigations were focused on the identification of reaction conditions that promote the formation of [1,3]dioxan-5-ols and suppress the formation of [1,3]dioxolan-4-yl-methanols.

Keywords: Solid acids; Glycerol; Acetalisation; Transacetalisation; Cyclic acetals

1. Introduction

Glycerol is obtained from the hydrolysis of fats into fatty acids and, recently, in large quantities in the production of biodiesel from rape oil. Due to this development, suitable uses for cheap glycerol from natural sources need to be found. A possible solution to the problem is the condensation of glycerol with aldehydes, ketones, or their dimethyl acetals to [1,3]dioxan-5-ols **1** and [1,3]dioxolan-4-yl-methanols **2** (isomeric 6- and 5-membered cyclic acetals) as novel fine chemical intermediates (Scheme 1).

According to their structure, the 6-membered ring acetals **1** derived from glycerol are potential precursors for the production of the "green" platform chemicals 1,3-dihydroxyacetone and 1,3-propanediol that might be obtained by subsequent selective oxidation or hyrogenation followed by acetal cleavage. But, unfortunately, the condensation of glycerol with aldehydes or ketones gives product mixtures with an excess of **2** or approximately equimolar amounts of **1** and **2** [1]. This phenomenon seems to be related to the nearly identical reactivity of the primary and secondary hydroxyl group in glycerol and to similar tendencies for the formation of the 5- and 6-membered rings in **2** and **1**. The direct separation of an isomer mixture **1** + **2** into their components obtained by the condensation of glycerol with acetaldehyde was carried out on a small scale with preparative gas chromatography [2]. An isolation of one or both of the compounds on a large scale is feasible by converting the mixed isomers **1** and **2** into derivatives with sufficiently different physical properties (i.e., boiling point, polarity, solubility). However, this procedure is disadvantageous because of expensive purification steps and results in considerable loss of the target product [3,4].

Up to now, the condensation of glycerol with aldehydes or ketones, and especially possible influences on the reaction product ratio **1**:**2**, have not yet been investigated systematically. Within the framework of our studies, we intended to identify the reaction conditions that influence the product composition. The main aspects of these investigations were monitoring (i) the reaction product formation and (ii) the variation of the reaction partner for glycerol. In a continuation of our earlier studies on heterogeneously catalysed aromatic acylations [5,6], we evaluated various solid acids as environmentally benign catalysts for the reaction.

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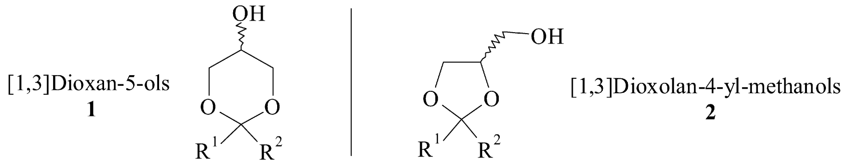


Scheme 1. The cyclic acetals formed in the condensation of glycerol with aldehydes or ketones.

2. Experimental

2.1. Chemicals

Glycerol (99+%), benzaldehyde (99+%), paraformaldehyde (95%), acetone (99+%), benzaldehyde dimethyl acetal (99%), formaldehyde dimethyl acetal (99%), acetone dimethyl acetal (98%), *p*-toluenesulphonic acid (98.5+%), toluene (99.8%), benzene (99.9+%), chloroform (99.9+%), and dichloromethane (99.9%) were purchased from Aldrich. The chemicals were used without further purification. The following solid acids were investigated as potential catalysts: Amberlyst-36 (an arenesulphonic acid polymer), Nafion-H NR-50 (a perfluoroalkanesulphonic acid polymer), and Montmorillonite K-10 (a clay mineral), purchased from Aldrich, and H-BEA (a zeolite, Si/Al = 25), purchased from Süd-Chemie.

The catalysts were pretreated before the experiments. Amberlyst-36 and Nafion-H NR-50 (beads) were dried at room temperature in an evacuated exsiccator over concentrated sulphuric acid instead of silica gel and swollen after the drying procedure overnight in the solvent used as a reaction medium. H-BEA and Montmorillonite K-10 were calcined at 500 and 200 °C, respectively, in air for 3 h.

2.2. Characterization of the solid acids used as catalysts

Specific surface areas and pore diameters were measured with nitrogen adsorption at −196 °C (ASAP 2000 system, Micromeritics). The acidities of H-BEA and Montmorillonite K-10 were characterised by temperature-programmed desorption (TPD) of ammonia (heat conductance detection), which was preadsorbed at 100 °C. The ammonia desorbed was quantified by reaction with 0.1 N sulphuric acid and back-titration.

2.3. Catalytic experiments

2.3.1. Condensation of glycerol with benzaldehyde (acetalisation)

The magnetically stirred (1000 rpm) reaction mixture (glycerol, aldehyde, solvent, and catalyst) was refluxed in a 100-mL flask with a condenser. A Dean–Stark trap was used to remove the formed water continuously. For monitoring the product formation and calculating the product yield, 0.45 g of hexamethylbenzene was added as an inert internal ^{1}H-NMR standard (CH_3:2.21 ppm in $CDCl_3$). Reaction samples (0.5 ml) were obtained periodically, filtered immediately through CELITE® 521 (catalyst separation from the hot mixture), cooled to room temperature, extracted with 0.5 mL of water to remove unreacted glycerol, dried with potassium carbonate, filtered again, and concentrated in vacuum to remove the solvent. The yields and isomer ratios of the formed cyclic acetals were determined by ^{1}H-NMR spectroscopy (solvent, $CDCl_3$). In addition, a sample of the pure product mixture (without the ^{1}H-NMR standard hexamethylbenzene) was prepared.

2.3.2. Condensation of glycerol with formaldehyde (source: paraformaldehyde) and acetone (acetalisation)

The reactions were carried out as described above, but without monitoring the product formation and thus in the absence of the ^{1}H-NMR-standard. After water separation was complete, the reaction mixtures were cooled to room temperature, filtered through CELITE® 521, and concentrated in vacuum. The remainders were purified by Kugelrohr distillation (boiling ranges: 75–100 °C at 7–8 mbar and 70–95 °C at 5–6 mbar). The yields of the acetal mixtures thus obtained were calculated from their weight, and the isomer ratios were analyzed by ^{1}H-NMR spectroscopy.

2.3.3. Condensation of glycerol with benzaldehyde dimethyl acetal, formaldehyde dimethyl acetal, and acetone dimethyl acetal (transacetalisation)

The reaction mixture (glycerol, dimethyl acetal of the respective carbonyl compound, dichloromethane/methanol as a solvent system, and catalyst) was magnetically stirred (1000 rpm) at room temperature in a closed 100-ml flask. To calculate the product yield, 0.45 g of hexamethylbenzene was added as an inert internal ^{1}H-NMR standard. Samples (0.5 ml) were obtained periodically from the dichloromethane phase, filtered through CELITE® 521, and concentrated in vacuum to remove the solvent. The yields and isomer ratios of the formed cyclic acetals were determined with ^{1}H-NMR spectroscopy (solvent, $CDCl_3$).

2.3.4. ^{1}H-NMR spectroscopic identification of the reaction products

Selected characteristic proton signals for the identification of the synthesised cyclic acetals **1a**–**2c** and **2a**–**2c** are compiled in Table 1. The measured chemical shifts are in agreement with previously published data [4,7–13].

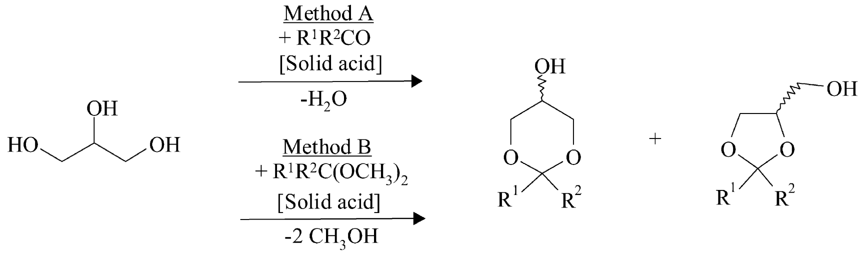
2.3.5. ^{1}H-NMR spectroscopic analysis of the product composition with varying temperature in presence of an acid

To 0.5 mmol of the acetal mixture (**1a** + **2a**: a prepared 61:39 mixture; **1b** + **2b**: a commercially available 58:42 mixture purchased from ACROS) 0.7 ml of toluene-d_8 was added as a solvent, followed by the addition of 0.01 mmol of *p*-toluenesulphonic acid. The samples were analyzed at 25, 40, 60, and 80 °C. The equilibrium in the samples was reached immediately after arriving the target temperature.

Table 1
The cyclic acetals **1a–1c** and **2a–2c** synthesised in the condensation of glycerol with benzaldehyde, formaldehyde, acetone or their dimethyl acetals and characteristic proton signals used for their identification and quantification with ^{1}H-NMR spectroscopy

Reactants	Formed cyclic acetals as reaction products	Compound no	Proton signal	Chemical shift (ppm)
Glycerol, benzaldehyde or benzaldehyde dimethyl acetal	(*E*)- and (*Z*)-2-phenyl-[1,3]dioxan-5-ol	(*E*)-**1a**, (*Z*)-**1a**	$OCH(C_6H_5)O$	5.53(s), 5.37(s)
	(*E*)- and (*Z*)-(2-Phenyl-[1,3]dioxolan-4-yl)-methanol	(*E*)-**2a**, (*Z*)-**2a**		5.80(s), 5.93(s)
Glycerol, formaldehyde or formaldehyde dimethyl acetal	[1,3]Dioxan-5-ol	**1b**	OCH_2O	4.78(d)[a], 4.91(d)[b]
	[1,3]Dioxolan-4-yl-methanol	**2b**		4.88(s), 5.06(s)
Glycerol, acetone or acetone dimethyl acetal	2,2-Dimethyl-[1,3]dioxan-5-ol	**1c**	$OC(CH_3)_2O$	1.44(d)[c], 1.46(d)[c]
	(2,2-Dimethyl-[1,3]dioxolan-4-yl)-methanol	**2c**		1.37(s), 1.44(s)

[a] $J = 6.2$ Hz.
[b] $J = 6.3$ Hz.
[c] $J = 0.6$ Hz.



1 + **2**

Method A: Aldehyde or ketone R^1R^2CO		Resulting reaction products		
Benzaldehyde:	$R^1 = C_6H_5$, $R^2 = H$	**1a**	+	**2a**
Formaldehyde:	$R^1 = R^2 = H$	**1b**	+	**2b**
Acetone:	$R^1 = R^2 = CH_3$	**1c**	+	**2c**

Method B: Dimethyl acetal $R^1R^2C(OCH_3)_2$		Resulting reaction products		
Benzaldehyde dimethyl acetal:	$R^1 = C_6H_5$, $R^2 = H$	**1a**	+	**2a**
Formaldehydedimethyl acetal:	$R^1 = R^2 = H$	**1b**	+	**2b**
Acetone dimethyl acetal:	$R^1 = R^2 = CH_3$	**1c**	+	**2c**

Scheme 2. Heterogeneously catalysed condensation of glycerol with benzaldehyde, formaldehyde, acetone (method A, acetalisation) or their dimethyl acetals (method B, transacetalisation) to mixtures of [1,3]dioxan-5-ols **1** and [1,3]dioxolan-4-yl-methanols **2**.

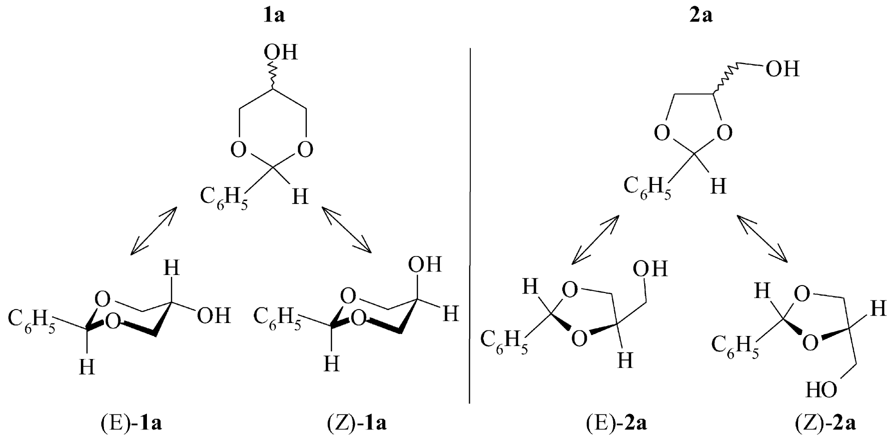
3. Results and discussion

3.1. Textural properties, acidities, and catalytic activity of various solid acids

The four catalytically investigated solid acids and their textural and acidic properties are listed in Table 2. The ion-exchanger resins Amberlyst-36 and Nafion-H NR-50 have small BET surface areas and sites of strong acidity (Brønsted sites: protons of sulphonic acid groups). In comparison, the inorganic solid acids H-BEA and Montmorillonite K-10 have considerable higher BET surface areas, but weaker acid sites (Lewis sites: Al ions, Brønsted sites: protons of Al ion coordinated hydroxyl groups). Amberlyst-36 contains the largest pores and the highest number of acid sites among these catalysts.

The solid acids were tested in the condensation of glycerol with benzaldehyde (Scheme 2, method A). The formation of water as a thermodynamically stable condensation product and its continuous removal from the reaction mixture (as an azeotropic mixture with the solvent) are strong driving forces for the reaction. All solid acids were catalytically active and produced the cyclic acetals **1a** (six-membered cyclic acetal) + **2a** (five-membered cyclic acetal) in yields >90% within few hours (Table 3) without side products. The required catalyst loading to achieve comparable reaction rates was significantly higher for H-BEA and Montmorillonite K-10 than for Amberlyst-36 and Nafion-H NR-50. The synthesised product mixture **1a** + **2a** contained the four conformational isomers (*E*)-**1a**, (*Z*)-**1a**, (*E*)-**2a**, and (*Z*)-**2a** shown in Scheme 3, which were identified with ^{1}H-NMR-spectroscopy (see Table 1).

Cooling the reaction mixture and their storage at room temperature over the solid catalysts gave a final product ratio **1a**:**2a** of about 60:40. Over Amberlyst-36 and H-BEA, this ratio was already achieved after standing overnight. Under the same conditions, the ratio was only 52:48 on Nafion-H NR-50 and 48:52 for Montmorillonite K-10. These ratios were conserved by removal of the solid acids with filtration. A final product ratio of about 60:40 was obtained on Nafion-H NR-50 and Montmorillonite K-10 only after few days (Table 3). The slow product



Scheme 3. Conformational isomers of **1a** and **2a**.

Table 2
Properties of various solid acids used as catalysts in the condensation of glycerol with benzaldehyde, formaldehyde, acetone, and their dimethyl acetals

Solid acid	BET surface area (m^2/g)	Average pore diameter (Å)	Number of acid sites (mmol/g)
Amberlyst-36	19	200	5.4[a,b]
Nafion-H NR-50 (beads)	<1	No pores	0.8[a]
H-BEA	500	7.6×6.4[c]	0.87[d,e]
Montmorillonite K-10	233	60	0.28[d,e]

[a] Ion exchange capacity according to product information.

[b] mmol/ml.

[c] Channels.

[d] From ammonia TPD.

[e] Sum of Lewis and Brønsted sites.

Table 3
Catalytic condensation of glycerol with benzaldehyde on various solid acids according to Scheme 2, method A[a]

Solid acid	Reaction time (h)	Yield of **1a** + **2a** (%)	Ratio **1a**:**2a** after cooling the reaction mixture and standing at room temperature
Amberlyst-36	4	94	61:39[b]
Nafion-H NR-50	4	94	52:48[b], 59:41[c]
H-BEA	6	94	59:41[b]
Montmorillonite K-10	6	95	48:52[b], 54:46[c], 59:41[d], 60:40[e]

[a] Reaction mixture: 0.11 mol glycerol, 0.1 mol benzaldehyde, 17.5 ml refluxing chloroform as the solvent, 0.1 g (Amberlyst-36, Nafion-H NR 50) or 1 g (H-BEA, Montmorillonite K-10) catalyst. The given yields are related to benzaldehyde.

[b] After standing overnight.

[c] After standing for 3 days.

[d] After standing for 7 days.

[e] After standing for 10 days.

Table 4
Catalytic condensation of glycerol with benzaldehyde dimethyl acetal at room temperature on various solid acids according to Scheme 2, method B[a]

Solid acid	Reaction time (h)	Yield of **1a** + **2a** (%)	Ratio **1a**:**2a**
Amberlyst-36	8	81	59:41
	24	82	60:40
Nafion-H NR-50	8	7	Not determined
	240	83	61:39
H-BEA	4	79	60:40
	24	80	61:39
Montmorillonite K-10	4	79	59:41
	24	79	60:40

[a] Reaction mixture: 0.1 mol glycerol, 0.11 mol benzaldehyde dimethyl acetal, 17.5 ml dichloromethane/1.5 ml methanol as solvent mixture, 0.5 g (Amberlyst-36, Nafion-H NR-50) or 2 g (H-BEA, Montmorillonite K-10) catalyst. The given yields are related to glycerol.

equilibration may be related to a hindered access (Nafion-H NR-50: low BET-area, no pores) and to a low number (Montmorillonite K-10) of acid surface sites (see Table 2).

The condensation of glycerol with benzaldehyde dimethyl acetal at room temperature (Scheme 2, method B) was used as a further probe reaction for the solid catalysts. A small amount of methanol was added to the solvent dichloromethane to increase the miscibility of the liquid components. With the exception of Nafion-H NR-50, all catalysts gave the product mixture **1a** + **2a** within a few hours in high yield (Table 4). The achieved ratios **1a**:**2a** of about 60:40 were the same, as for the condensation according to method A (analysed for the product mixtures cooled over the catalysts; see Table 3).

Due to the high activity and the low amounts to be used for the glycerol condensations, Amberlyst-36 was selected as the catalyst for the investigations reported in the following sections.

3.2. *Catalytic condensation of glycerol with benzaldehyde*

The condensation of glycerol with benzaldehyde to **1a** + **2a** was performed on the catalyst Amberlyst-36 at varying reaction temperatures in different solvents (Table 5). The reaction temperature increased in the final phase of the experiments (completed water formation) from the boiling point of the azeotropic mixture solvent/water to the boiling point of the pure solvent. An extended reaction time was necessary to achieve a high educt conversion in the low boiling solvent dichloromethane.

The catalytic experiments showed a significant dependence of the final product ratio **1a**:**2a** on the reaction temperature. It was found that the formation of the six-membered cyclic acetal

Table 5
Catalytic condensation of glycerol with benzaldehyde on Amberlyst-36 at varied reaction temperature according to Scheme 2, method A[a]

Reaction temperature (°C)	Solvent	Reaction time (h)	Yield of **1a** + **2a** (%)	Final ratio **1a**:**2a** in the reaction mixture at reaction temperature	Ratio **1a**:**2a** after cooling the reaction mixture and standing overnight at room temperature
84.1–110.8	Toluene	2	94	33:67	61:39
69.3–80.0	Benzene	2	87	37:63	61:39
56.1–61.2	Chloroform	4	94	44:56	61:39
38.1–40.0	Dichloromethane	14	80	62:38	62:38

[a] Reaction mixture: 0.11 mol glycerol, 0.1 mol benzaldehyde, 17.5 ml refluxing solvent, 0.1 g (reactions in toluene, benzene, and chloroform) or 0.5 g (reaction in dichloromethane) Amberlyst-36 as the catalyst. The given yields are related to benzaldehyde.

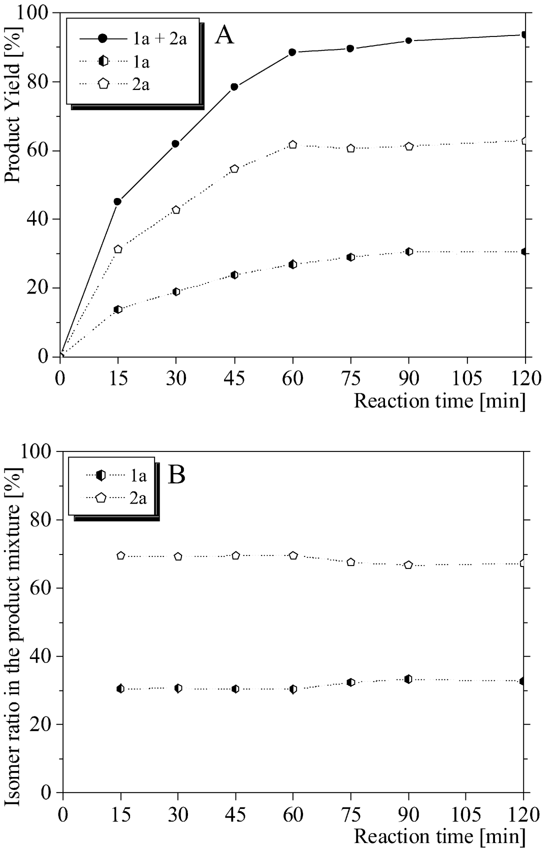


Fig. 1. Kinetics of the Amberlyst-36-catalysed condensation of glycerol with benzaldehyde in refluxing toluene (A) and ratios of the formed reaction products **1a** and **2a** over the reaction time (B).

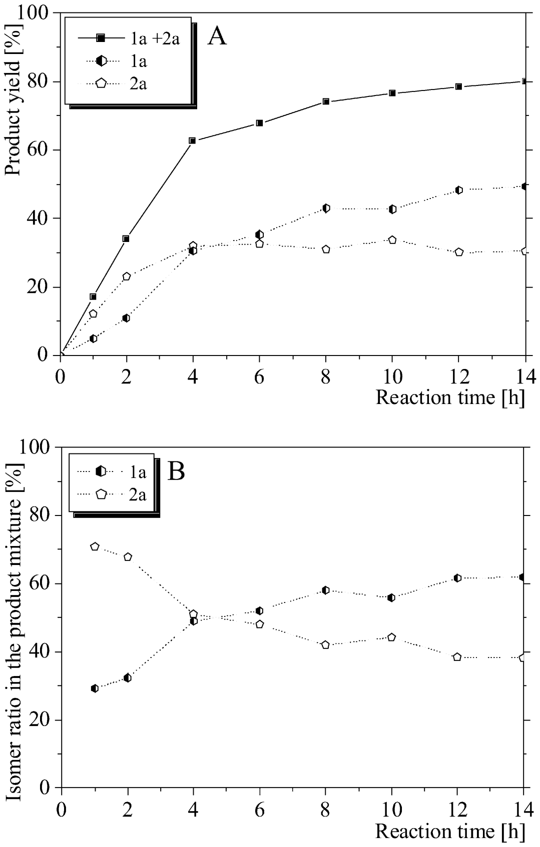


Fig. 2. Kinetics of the Amberlyst-36-catalysed condensation of glycerol with benzaldehyde in refluxing dichloromethane (A) and ratios of the formed reaction products **1a** and **2a** over the reaction time (B).

1a is favoured by mild thermal conditions. In agreement with the experiments reported in the previous section, an unique ratio **1a**:**2a** of about 60:40 was obtained after the reaction mixtures were cooled over the catalyst to room temperature and allowed to stand overnight.

The catalytic condensation of glycerol with benzaldehyde in the solvents toluene and dichloromethane were monitored over time to investigate the influence of the reaction temperature on the product ratio in more detail. According to Fig. 1A, the reaction was nearly complete after 2 h in the high-boiling point solvent toluene, whereas the ratio **1a**:**2a** remained nearly constant the whole time. The quantity of **1a** increased only marginally at the expense of **2a** in the final reaction phase (Fig. 1B). In the low-boiling point solvent dichloromethane, a product yield of 80% was achieved after 14 h (Fig. 2A). In the course of the reaction, the quantity of **1a** increased significantly at the expense of **2a** (Fig. 2B). Independent of the reaction temperature, the condensation occurred in two stages. During the first, and, kinetically controlled stage, the catalytic formation of the five-membered cyclic acetal **2a** proceeds at a higher rate than that of the six-membered cyclic acetal **1a**. An acid-catalysed temperature-dependent equilibrium between **1a** and **2a** (ring transformation) at high conversion degree is characteristic for the second, thermodynamically controlled stage of the reaction.

The existence of a temperature-dependent acid-catalysed equilibrium between **1a** and **2a** was verified with an NMR experiment. *p*-Toluenesulphonic acid, the soluble analogue of

Amberlyst-36, was used as the catalyst for equilibration in the solvent toluene-d_8. Fig. 3 shows an increasing quantity of **2a** and, consequently, a decreasing quantity of **1a** in the product mixture with increasing temperature. In absence of any acid, the ratio **1a**:**2a** remained constant. Scheme 4 proposes a ring-transformation process for the observed acid-catalysed equilibration. The postulated benzyl cation (positive charge stabilised by the phenyl substituent) is a plausible key intermediate of this ring transformation.

3.3. Catalytic condensation of glycerol with formaldehyde and acetone

Glycerol was reacted catalytically on Amberlyst-36 with paraformaldehyde (solid polymeric formaldehyde) as a water-free and easily handled solid source of formaldehyde, to give a mixture of the cyclic acetals **1b** and **2b** (see Scheme 2). Regrettably, the distinct inhomogeneity of the reaction mixture at low and moderate conversion degrees made analytical monitoring of the product formation impossible. Generally, the condensation of glycerol with formaldehyde showed a higher tendency to form the six-membered cyclic acetal than did that with benzaldehyde. A decreased reaction temperature was beneficial in increasing the quantity of **1b** in the product mixture (Table 6).

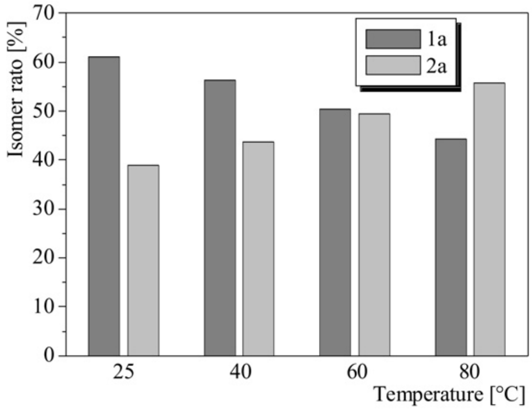


Fig. 3. Varying composition of a **1a** + **2a** mixture with the temperature in presence of a catalytic amount of p-toluenesulphonic acid.

To the best of our knowledge, the ratios **1b**:**2b** achieved are higher than those obtained up to now for the reaction of glycerol with formaldehyde (40:60, 56:44) [9,10,14]. An acetal mixture **1b** + **2b** with a ratio of 96:4 was prepared in a two-step reaction (synthesis of 3-methoxymethoxy-propane-1,2-diol and its subsequent cyclisation) [9]. However, this synthetic procedure is complicated, difficult to reproduce, and suited only for small-scale production.

The ratios **1b**:**2b** in the hot and cooled reaction mixtures were identical over the solid catalyst. Likewise, the repetition of the acid-catalysed NMR experiment (see Fig. 3) with the mixture **1b** + **2b** also showed no influence of temperature on its composition. Thus, the final thermodynamically controlled reaction stage found for the reaction of glycerol with benzaldehyde is unlikely for the reaction of glycerol with formaldehyde. Due to the absence of any stabilising substituent, an equilibration between **1b** and **2b** via ring transformation is not favoured. Obviously, the formation of **1b** and **2b** in different quantities is kinetically controlled.

Table 6

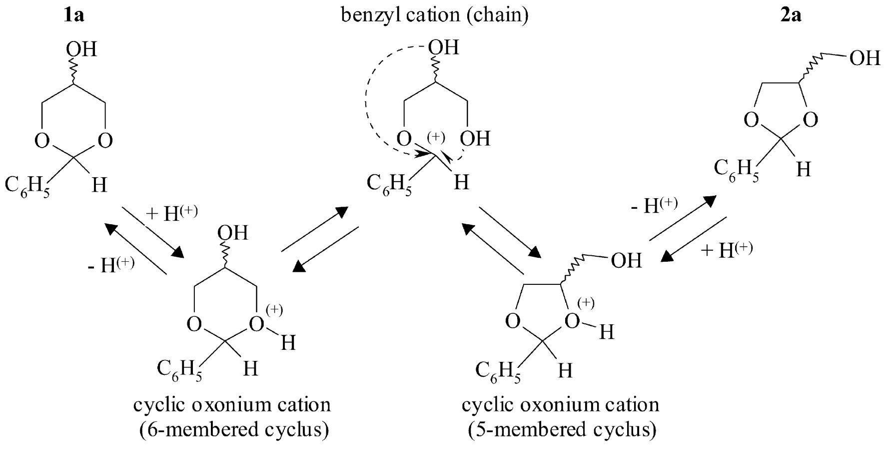
Catalytic condensation of glycerol with formaldehyde and acetone on Amberlyst-36 according to Scheme 2, method A[a]

Carbonyl compound	Reaction temperature (°C)	Solvent	Reaction time (h)	Yield of **1** + **2** (%)	Ratio **1**:**2**
Formaldehyde	84.1–110.8	Toluene	2	58[b]	65:35[b]
	69.3–80.0	Benzene	4	62[b]	68:32[b]
	56.1–61.2	Chloroform	6	77[b]	76:24[b]
	38.1–40.0	Dichloromethane	14	74[b]	78:22[b]
Acetone	38.1–40.0	Dichloromethane	8	88[c]	<1:99[c]

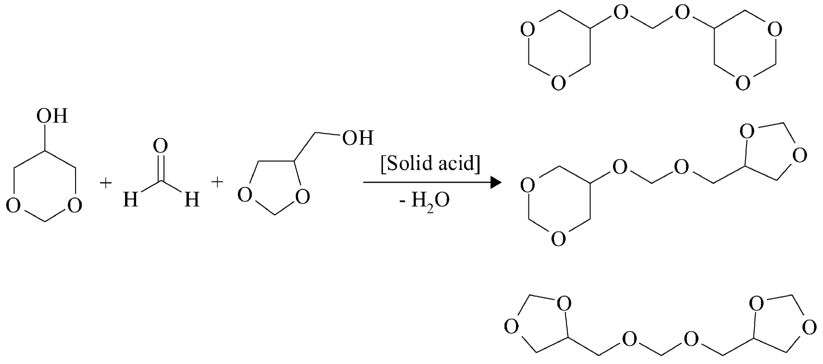
[a] Reaction mixture for the acetalisation of formaldehyde: 0.11 mol glycerol, paraformaldehyde corresponding to an amount of 0.1 mol formaldehyde, 17.5 ml refluxing solvent, 0.1 g (reactions in toluene and benzene), 0.5 g (reaction in chloroform), or 1 g (reaction in dichloromethane) Amberlyst-36 as the catalyst. The given yields are related to formaldehyde. Reaction mixture for the acetalisation of acetone: 0.1 mol glycerol, 0.15 mol acetone, 17.5 ml refluxing dichloromethane, 0.5 g Amberlyst-36 as the catalyst. The given yield is related to glycerol.

[b] **1** = **1b**, **2** = **2b** (according to Scheme 1).

[c] **1** = **1c**, **2** = **2c** (according to Scheme 1).

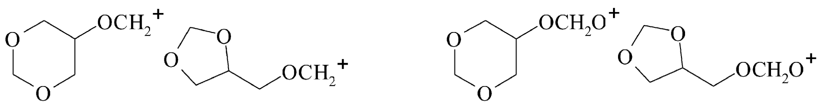


Scheme 4. Acid-catalysed equilibrium between **1a** and **2a** (ring transformation).



1b **2b** Consecutive products

Scheme 5. Heterogeneously catalysed consecutive reactions of the cyclic acetals **1b** and **2b** with formaldehyde and their possible products.



$C_5H_9O_3^+$, mass number 117 $C_5H_9O_4^+$, mass number 133

Scheme 6. Mass spectroscopically detected fragments of the consecutive products formed according to Scheme 5.

Regardless of the total formaldehyde conversion achieved, the yields of **1b** + **2b** were observed to decrease at high temperatures (Table 6, experiments in benzene and toluene). For these experiments, the removal of **1b** + **2b** from the crude product by distillation left a liquid remainder. It contained a second fraction with a higher boiling range (145–170 °C at 9–11 mbar). The GC-MS analysis of this distillate revealed three components (ratio 35:51:14), which may result from the thermally favoured consecutive reaction of **1b** and **2b** with formaldehyde presented in Scheme 5. The mass spectra of the three side products are nearly identical and exhibit fragments with mass numbers of 117 and 133, but no mol peaks. The detected fragments and their possible structures shown in Scheme 6 are in agreement with the consecutive products given in Scheme 5.

The homogeneously catalysed condensation of glycerol with acetone is known to produce the five-membered ring acetal **2c** (Scheme 2) with high yield [15–18]. Only one paper has reported the additional formation of the six-membered ring acetal **1c** in low amounts [19]. The reaction over the heterogeneous catalyst Amberlyst-36 gave **2c** without any detectable amounts of **1c** (see Table 6).

The prepared cyclic acetals **1b**, **2b**, and **2c** are water-soluble compounds. Their synthesis on the solid, easily separable acid Amberlyst-36 avoids an extractive catalyst removal with aqueous alkali from the reaction mixture and resulting product losses.

3.4. Catalytic condensation of glycerol with the dimethyl acetals of benzaldehyde, formaldehyde, and acetone

Aldehydes and ketones, which are sensitive toward oxidation or an acid-catalysed self-condensation, are often substituted in organic syntheses for their dimethyl acetals as more stable reactants. Correspondingly, glycerol can successfully be reacted on homogeneous catalysts with the dimethyl acetals of benzaldehyde and acetone [20–22]. In our experiments, the heterogeneous catalyst Amberlyst-36 was used for the condensations of glycerol with benzaldehyde dimethyl acetal, formaldehyde dimethyl acetal, and acetone dimethyl acetal (see Scheme 2, method B).

Table 7
Catalytic condensation of glycerol with various dimethyl acetals on Amberlyst-36 at room reaction temperature according to Scheme 2, method B[a]

Dimethyl acetal	Reaction time (h)	Yield of **1** + **2** (%)	Ratio **1**:**2**
Benzaldehyde dimethyl acetal	8 24	81[b] 82[b]	59:41[b] 60:40[b]
Formaldehyde dimethyl acetal	24	0[c]	–
Acetone dimethyl acetal	1.5 24	76[d] 84[d]	<1:99[d] <1:99[d]

[a] Reaction mixture: 0.1 mol glycerol, 0.11 mol dimethyl acetal, 17.5 ml dichloromethane/1.5 ml methanol as solvent mixture, 0.5 g Amberlyst-36 as the catalyst. The given yields are related to glycerol.

[b] **1** = **1a**, **2** = **2a** (according to Scheme 1).

[c] **1** = **1b**, **2** = **2b** (according to Scheme 1).

[d] **1** = **1c**, **2** = **2c** (according to Scheme 1).

Glycerol reacted on the solid acid with benzaldehyde dimethyl acetal and acetone dimethyl acetal already at room temperature to give **1a** + **2a** and **2c**, respectively, in high yield. In contrast, formaldehyde dimethyl acetal exhibited no reactivity under the same conditions (Table 7).

The condensation of glycerol with benzaldehyde dimethyl acetal was monitored over time and showed a long induction period (Fig. 4A). The low reaction rate observed for this interval was related to poor miscibility of glycerol with the mixture benzaldehyde dimethyl acetal/solvent at room temperature.

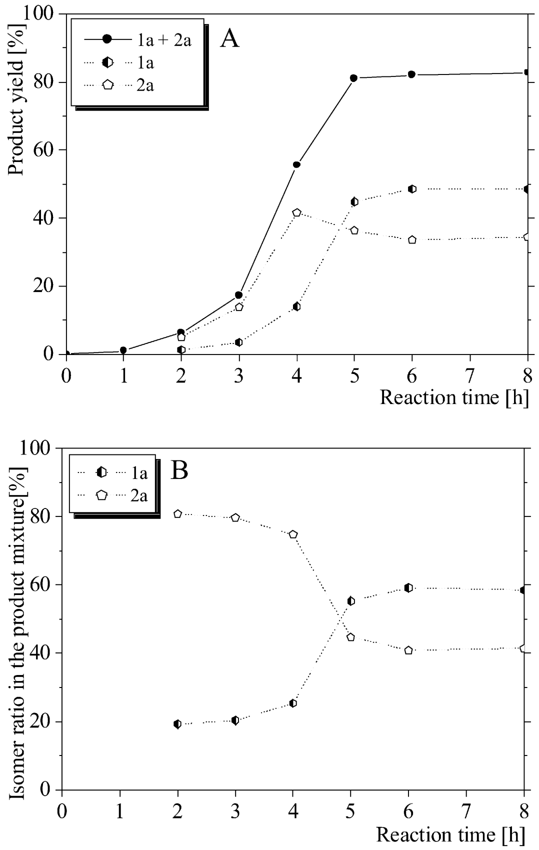


Fig. 4. Kinetics of the Amberlyst-36-catalysed condensation of glycerol with benzaldehyde dimethyl acetal at room temperature in dichloromethane (A) and ratios of the formed reaction products **1a** and **2a** over the reaction time (B).

With progressing formation of the reaction product methanol, the two liquid phases of the reaction mixture became completely miscible. From this point, the reaction rate increased significantly, passed a maximum, and then decreased at high conversion degree. In principal, the transacetalisation of glycerol with benzaldehyde dimethyl acetal had the same reaction stages (i.e., rapid formation of **2a** followed by an equilibration of the product mixture **1a** + **2a** in favour of **1a**) as the acetalisation of glycerol with benzaldehyde in dichloromethane reported in Section 3.2. In further agreement, the reaction product composition changed similarly over the time and reached the same final ratio **1a**:**2a** of about 60:40 (Fig. 4B).

4. Conclusion

The catalytic condensation of glycerol with benzaldehyde, formaldehyde, and acetone can be carried out on Amberlyst-36 and other solid acids as environmentally friendly catalysts to give cyclic acetals in high yields. Reactions of glycerol with benzaldehyde and formaldehyde on Amberlyst-36 produce mixtures of [1,3]dioxan-5-ols (6-membered cyclic acetals as novel precursors for 1,3-propanediol derivatives) and [1,3]dioxolan-4-yl-methanols (5-membered cyclic acetals). A mild reaction temperature is beneficial to increase the quantity of the desired 6-membered cyclic acetal in the mixture. High ratios (up to 78%) can be achieved for this compound type with formaldehyde (source: paraformaldehyde) as a reaction partner for glycerol. In contrast, the condensation of glycerol with acetone gives the 5-membered cyclic acetal exclusively.

The mixture of the 5- and 6-membered cyclic acetals derived from the reaction of glycerol with benzaldehyde at different temperatures shows a varying composition in presence of an acid. This phenomenon is probably related to a catalytic ring transformation, which is not observed for the mixture of the 5- and 6-membered cyclic acetal derived from the reaction of glycerol with formaldehyde.

The dimethyl acetals of benzaldehyde and acetone can be used for Amberlyst-36-catalysed condensation with glycerol as alternative reactants to the free carbonyl compounds and will give the cyclic acetals at the same ratios. As an exception, formaldehyde dimethyl acetal exhibits a significantly lower, and thus insufficient, reactivity for the reaction with glycerol.

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References

[1] A.J. Showler, P.A. Darley, Chem Rev. 67 (1967) 427.
[2] G. Aksnes, P. Albriktsen, P. Juvvik, Acta Chem. Scand. 19 (1965) 920.
[3] P.H.J. Carlsen, K. Soerbye, T. Ulven, K. Aasboe, Acta Chem. Scand. 50 (1996) 185.
[4] S. Bartoli, G. De Nicola, S. Roelens, J. Org. Chem. 68 (2003) 8149.
[5] J. Deutsch, A. Trunschke, D. Müller, V. Quaschning, E. Kemnitz, H. Lieske, J. Mol. Catal. A 207 (2004) 51.
[6] J. Deutsch, H.A. Prescott, D. Müller, E. Kemnitz, H. Lieske, J. Catal. 231 (2005) 269.
[7] Y. Suhara, H. Takayama, S. Nakane, T. Miyashita, K. Waku, T. Sugiura, Chem. Pharm. Bull. 48 (2000) 903.
[8] F. Marguet, J.F. Cavalier, R. Verger, G. Buono, Eur. J. Org. Chem. 7 (1999) 1671.
[9] J.L. Gras, A. Poncet, Bull. Soc. Chim. Fr. 128 (1991) 566.
[10] G.T. Teregulova, L.Z. Rolnik, S.S. Zlotskii, D.L. Rakhmankulov, Zh. Prikl. Khim. 64 (1991) 1591.
[11] D.A. Predvoditelev, M.A. Malenovskaya, E.E. Nifantev, Zh. Obshch. Khim. 68 (1998) 931.
[12] D.C. Forbes, D.G. Ene, M.P. Doyle, Synthesis (1998) 879.
[13] A. Krief, A. Froidbise, Tetrahedron 60 (2004) 7637.
[14] J.L. Gras, R. Nougier, M. Mchich, Tetrahedron Lett. 28 (1987) 6601.
[15] T. Cablewski, A.F. Faux, C.R. Strauss, J. Org. Chem. 59 (1994) 3408.
[16] K. Matsumoto, S. Fuwa, M. Shimojo, H. Kitajima, Bull. Chem. Soc. Jpn. 69 (1996) 2977.
[17] P. Sahai, R.A. Vishwakarma, J. Chem. Soc. Perkin Trans. 1 12 (1997) 1845.
[18] A. Krief, L. Provins, A. Froidbise, Tetrahedron Lett. 39 (1998) 1437.
[19] D.Y. He, J. Zhan, Z.J. Li, Y.Q. Liu, D.X. Xiu, M.S. Cai, Synth. Commun. 22 (1992) 2653.
[20] C. Piantadosi, C.E. Anderson, E.A. Brecht, C.L. Varbro, J. Am. Chem. Soc. 80 (1958) 6613.
[21] F. Gorla, L.M. Venenzi, Helv. Chim. Acta 73 (1990) 690.
[22] M.W. Chun, D.H. Shin, H.R. Moon, J. Lee, H. Park, L.S. Jeong, Bioorg. Med. Chem. Lett. 7 (1997) 1475.