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Towards a Sustainable Synthesis of Oxymethylene Dimethyl Ether by Homogeneous Catalysis and Uptake of Molecular Formaldehyde

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TOC Graphic and Short Text

OME^{*n*} **goes green?** A novel oxymethylene dimethyl ether (OME_{*n*}) synthesis from dimethoxymethane and monomeric gaseous formaldehyde is reported. This anhydrous synthesis route catalyzed homogenously by trimethyloxonium salts represents a new approach towards a sustainable synthesis of oxymethylene dimethyl ethers from green starting materials.

Keywords: Oxymethylene dimethyl ethers – Homogeneous catalysis – Molecular formaldehyde – Weakly coordinating anion – NMR spectroscopy.

Abstract: Oxymethylene dimethyl ethers (OME_n; $CH_3(-OCH_2-)_nO-CH_3$, n = 3-5) are a novel class of sustainable synthetic fuels, which are of increasing interest due to their soot-free combustion. Herein a novel anhydrous OME_n synthesis route is presented. Catalyzed by trimethyloxonium salts, dimethoxymethane takes up monomeric gaseous formaldehyde instantaneously and forms high purity OME_n at temperatures of 25 - 30 °C. This new anhydrous approach using molecular formaldehyde and catalytic amounts of highly active trimethyloxonium salts represents a promising new step towards a sustainable formation of OME_n emanating from CO₂ and H₂.

Oxymethylene dimethyl ethers (OME_n) of the general formula $CH_3(-OCH_2-)_nO-CH_3$ are a novel class of non-toxic compounds, which attract increasing interest due to their versatile applications. With their diesel-like properties in combination with soot-free combustion, OME_n are considered as diesel additives or even as a novel class of synthetic fuels (for n = 3-5).^[1] In addition, OME_n are discussed as solvents or for the absorption of CO_2 .^[2] For OME_n formation, two structural building units are necessary: On the one hand molecules are required, which extend the oxymethylene chain by providing CH₂O-units (e.g. para-formaldeyhde (para-FA), 1,3,5-trioxane (TRI)). On the other hand, molecules are needed, which contain methoxy groups for the chain termination (e.g. methanol, dimethoxymethane, dimethyl ether). Currently, established OME_n syntheses are either based on aqueous syntheses routes via the reaction of methanol (MeOH) and a FA-source, or anhydrous by the reaction of dimethoxymethane (OME₁) and TRI.^[3-12] However, the synthesis of dry TRI is complex and very energy demanding. In addition, the presence of water in OME_n syntheses initiates the formation of large amounts of side-products^[13] and OME_n conversion decreases with increasing water content. The product separation for aqueous syntheses routes is evolving,^{*} but remains a very energyintensive key step largely increasing the CO_2 footprint of the thereby produced OME_n (ca. 7 -10 MJ kg⁻¹; this constitutes $\frac{1}{2}$ to $\frac{1}{2}$ of the lower heating value of OME₁₋₆ of *ca*. 19-22 MJ kg⁻¹). To counteract these disadvantages, we set out to evolve a sustainable and anhydrous synthesis route starting from CO₂ and H₂. In previous work, we established highly reliable thermodynamic data for the OME_n formation in gas and condensed phase (Table 1).^[14]

Reaction	∆ _r H°(gas) / kJ mol ⁻¹	∆ _r G°(gas) / kJ mol ⁻¹	∆ _r G°(liquid) / kJ mol ^{−1}
$CO_2 + 3 H_2 \rightarrow H_3C-OH + H_2O$	-49.3	+3.5	_
$H_3C-OH \rightarrow H_2C=O + H_2$	+92.4	+59.7	-
$2 H_3C-OH \rightarrow DME^{a)} + H_2O$	-23.9	-16.6	-
$DME^{a)} + H_2C=O \rightarrow OME_1$	-55.5	-	-21.3
$OME_1 + H_2C=O \rightarrow OME_2$	-53.4	_	-15.3
$OME_2 + H_2C=O \rightarrow OME_3$	-53.9	_	-16.3
$OME_3 + H_2C=O \rightarrow OME_4$	-53.7	_	-16.1
$OME_4 + H_2C=O \rightarrow OME_5$	-53.8	_	-16.0

Table 1: Thermodynamic data for the OME_n formation starting with CO₂ and H₂. Data extracted from ^[14].

^{a)} DME = $O(CH_3)_2$ – dimethyl ether.

From Table 1, OME_n synthesis, starting from DME or OME₁ and n molecular monomeric FA (best from dehydrogenation of methanol), is thermodynamically viable ($\Delta_r G^{\circ}(\text{liquid}) = -21.3 / -15.3 \text{ kJ mol}^{-1}$).

^{*} Prof. Dr.-Ing. J. Burger, "OME Technology made in Germany, 25.01.2017", can be found under http://www.ome-technologies.de/fileadmin/omet/OMETechnologiesGmbH_Jan2017.pdf.

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According to our previously published thermodynamic evaluation,^[5,14] this represents energetically the most efficient route to OME_n. Overall, starting from green CO₂ / H₂, it follows the path CH₃OH, DME, followed by the reaction with monomeric FA to give the desired liquids in an anhydrous route with 22 % less H₂ used than on the conventional route via trioxane.^[5] Herein we demonstrate such an OME_n synthesis based on OME₁ and FA (Eq. 1). In contrast to previously reported literature and known syntheses,^[3-11] where FA-sources (e.g. TRI, *para*-FA, FA (aq)) are used, we employ monomeric FA. Catalyzed by trimethyloxonium salts OMe₃⁺[X]⁻ (X = BF₄; Al(OR^F)₄ with OR^F = OC(CF₃)₃), these reactions proceed at ambient temperatures, instantaneously take up the continuously introduced FA and form OME_n (*n* = 2-6; *ca*. 99 %) with only about 1 % of TRI-impurities (Eq. 1).

$$\bigcirc \bigcirc \bigcirc \bigcirc \bigcirc + n$$
 $\stackrel{\bigcirc}{\underset{H \longrightarrow H}{\longrightarrow}} \xrightarrow{\text{cat. OMe}_3^+[X]^-} \bigcirc \bigcirc \bigcirc \bigcirc \bigcirc \bigcirc \bigcirc \bigcirc \xrightarrow{n+1}$ (Eq. 1)

Depending on the OME₁/TRI-ratio and temperature, classical OME_n syntheses produce equilibrium mixtures of the starting materials (OME₁, TRI) and higher OME_n ($n \ge 2$) (Flory-Schulz-distribution). According to the law of mass action, the ratio OME_n/OME_{n-1} is proportional to the partial pressure of FA. In established anhydrous synthesis routes, this partial pressure is determined by TRI exclusively. Based on the similar equilibrium constants for the reaction OME_{n-1(I)} + FA_(g) \rightleftharpoons OME_{n(I)} (where n > 2,^[15]) and the low FA-partial pressure of TRI at the reaction temperature (e.g. 4.2 mbar at 25 °C, calculated using thermodynamic data from Ref. [16]), the contribution of higher OME_n declines exponentially. However, the use of higher FA-partial pressures (*ca*. 8 mbar) would be sufficient to make higher OME_n-chains thermodynamically more favorable than TRI.

To run the reaction using monomeric FA and thus to eliminate the Flory-Schulz product distribution, we developed a FA generator, which provides a continuous flow of monomeric gaseous FA (5 – 26 Vol.% in N₂ and 7 – 36 mmol h⁻¹ respectively; ESI Section 1). This monomeric FA-stream was introduced into liquid OME₁ at 25 to 30 °C. OME_n formation was catalyzed by 0.8 to 3.0 mol.% of dissolved Me⁺-donor OMe₃⁺[X]⁻. To understand the influence of [X]⁻ counterion, and to demonstrate the use of a commercially available catalyst, OMe₃⁺[BF₄]⁻ with a smaller (V^- = 0.079 nm³) more coordinating counterion was used as a benchmark catalyst.^[17] In addition, we prepared, fully characterized and tested novel OMe₃⁺[Al(OR^F)₄]⁻ with a very large (V^- = 0.755 nm³) and very weakly coordinating anion (WCA; see ESI - Section 2).^[18] The [Al(OR^F)₄]⁻ WCA typically induces solubility also in low polarity solvents.^[19]

Catalysis with OMe₃⁺[**BF**₄]⁻: Initial experiments were performed by using catalytic amounts of OMe₃⁺[**BF**₄]⁻ in OME₁ at 25 °C. Due to the low solubility of OMe₃⁺[**BF**₄]⁻ in OME₁ the introduced FA preferentially polymerizes to a *para*-FA precipitate, instead of extending the OME_n chain. However, by adding acetonitrile (OME₁:acetonitrile = 0.5 v/v), this problem is overcome and the preferential formation of higher OME_n (n = 2-6; *Exp. 1a, 1b*) was observed. The product mixtures were analyzed by 2D-NMR-spectroscopy and OME_n selectivities ($n \ge 2$) were determined by integration of the proton-NMR-signals (ESI - Section 3). A complete NMR characterization of the pure OME_n (OME₁₋₄) is provided in the ESI (Section 4) and an exemplary OME_n mixture analysis by NMR is compared with gas chromatographic measurements leading to consistent results in OME_n selectivity (ESI - Section 5).

Compatibility of OMe₃⁺[**BF**₄]⁻ **and MeCN**: To elucidate the question, if OMe₃⁺[**BF**₄]⁻ is the active Me⁺donor in acetonitrile, both were reacted in the absence of OME₁. NMR spectra of OMe₃⁺[**BF**₄]⁻ in acetonitrile-d₃, demonstrated that acetonitrile was quantitatively methylated to [Me-C=N-Me]⁺[**BF**₄]⁻. In addition, this known compound^[20] was prepared and fully characterized (ESI - Section 6). Probably this compound forms the catalytically active species that acts as a Me^+ donor and catalyzes the OME_n formation in the presence of acetonitrile (see below for mechanistic investigations).

Catalysis with OMe₃⁺[**Al**(**OR**^F)₄]⁻: Experiments with pure OME₁ and catalytic amounts of OMe₃⁺[BF₄]⁻ led to FA-polymerization instead of FA-uptake. Yet, catalysis without the addition of MeCN solvent would be very desirable. To increase the catalytic efficiency of the OMe₃⁺ source, the synthesized OMe₃⁺[Al(OR^F)₄]⁻ was used. With this perfluorinated anion, an enhanced solubility is achieved and the catalytic activity of a more "naked" OMe₃⁺ cation is increased. The addition of only 0.8 mol.% catalyst (with respect to OME₁) resulted in an instantaneous uptake of the introduced FA (*ca*. 0.5 mmol min⁻¹) for the formation of OME_n. The increase in catalytic efficiency was confirmed by NMR-analyses of the reaction mixture before and after quenching (Figure 1).



Figure 1: ¹H NMR spectra (400.17 MHz) of the reaction mixture of OME₁ and FA (molar ratio = 1.8:1) with 0.8 mol.% OMe₃⁺[Al(OR^F)₄]⁻ before and after quenching with Na[OMe]. Measurements were performed at T = 25 °C.

The ¹H NMR-spectrum before quenching with Na[OMe] shows two broad resonances at δ = 3.65 ppm and in the range of δ = 4.2 - 5.0 ppm, which relate to the methoxy and oxymethylene groups of the different OME_n. This demonstrates effective intermolecular exchange of all the molecular building blocks below the millisecond NMR-timescale. In contrast, the proton spectrum after quenching with Na[OMe] shows sharp singlet peaks, which can be assigned to the protons of OME_n (n = 1-6).

Analysis of the OME_n Yields and Selectivity: The molar ratio of the generated OME_n (n = 2-6) for the syntheses with OMe₃⁺[BF₄]⁻ in acetonitrile and OMe₃⁺[Al(OR^F)₄]⁻ in pure OME₁ are summarized in Figure 2. Interestingly, the selectivity for OME_n (n > 2) with catalytic amounts of OMe₃⁺[Al(OR^F)₄]⁻ is, despite of the lower molar ratio (OME₁:FA = 1.8), larger than the ratios obtained with OMe₃⁺[BF₄]⁻ in acetonitrile (OME₁:FA = 1.0; 1.5). This illustrates a higher selectivity for OME_{n>2} with OMe₃⁺[Al(OR^F)₄]⁻. By-products are methyl formate (MF; $\delta = 3.68$ ppm, d, ⁴J_{HH}=0.8 Hz; 8.02 ppm, q, ⁴J_{HH}=0.8 Hz), dimethyl ether ($\delta = 3.22$ ppm, s) and traces of TRI ($\delta = 5.07$ ppm, s). However, the TRI content was <1 mol.% and the formation of MF presumably arises due to the side reaction of OME₁ upon prolonged exposure to OMe₃⁺[Al(OR^F)₄]⁻ (ESI Section 7). The existence of small amounts of DME results partially from the quenching of OMe₃⁺[Al(OR^F)₄]⁻ with Na[OMe] or additionally from a partial

OME₁ dismutation.

In addition, the expected OME_n selectivity was calculated based on a vapor-liquid-equilibrium model described in Ref. [5]. The simulation confirms the experimentally obtained product ratios (Figure 2).



Figure 2: Experimental and simulated OME_n-selectivity for the different OME₁:FA-ratios and catalysts.

DFT-Investigations towards a Hypothetic Reaction Mechanism: To obtain a deeper understanding of the occurring reactions, a cycle for the OME_n formation catalyzed by the trimethyloxonium cation was calculated with dispersion corrected density functional theory (DFT) methods (BP86 (D3BJ)/def-TZVP; ESI - Section 8). The methylation of OME₁ can be expected to initiate the formation of the catalytically active species **1** in an exergonic reaction ($\Delta_r G^0 = -24$ kJ mol⁻¹, **A**; Figure 3). After cleavage of DME, the generated oxocarbeniumion is stabilized by resonance (see box in Figure 3).



Figure 3: Catalytic Cycle for the formation of OME_n with OMe_3^+ -Catalysts starting from OME_1 and FA. Thermodynamic data was calculated with BP86 (D3BJ)/def-TZVP for n = 1. All values are given in kJ mol⁻¹.

By nucleophilic attack of FA, the elongation of the OME_n chain takes place and an oxocarbenium-ion **2** and DME are formed in an endergonic reaction ($\Delta_r G^0 = +38 \text{ kJ mol}^{-1}$, **B**). These two compounds react exergonic by nucleophilic attack of the released DME (or an OME_n molecule nearby) and

formation of the dimethyloxonium cation **3** ($\Delta_r G^0 = -52 \text{ kJ mol}^{-1}$, **C**). By transferring a methyl group from **3** to OME₁ the catalytically active species **1** is regenerated and the higher OME_n is formed ($\Delta_r G^0 = +10 \text{ kJ mol}^{-1}$, **D**). The calculated energy profile for this process is viable and in very good agreement with the experiment. In accordance with the rapid exchange on the NMR time scale (Figure 1), one expects that the barriers for the processes **A** to **D** to be low.

In summary, a novel anhydrous synthesis of oxymethylene dimethyl ethers (OME) based on the reaction of monomeric FA and OME₁ was established. By the use of the highly active salt $OMe_3^+[Al(OR^F)_4]^-$ in pure OME₁ an instantaneous uptake of the introduced FA was observed accompanied by the formation of OME_n (*ca*. 99%) with marginal TRI impurities (*ca*. 1%). The experiments were confirmed by comparison with simulations, and a catalytic cycle was proposed and supported by DFT calculations. To use OME_n as sustainable synthetic fuels on a large scale, the high catalytic activity in combination with the selective formation of higher OME_n is crucial. Here OME₁ served as a model substance. Future investigations will be carried out on the reaction of DME and FA. Moreover, catalyst recycling is essential and ongoing work is performed in our laboratories. In addition, the process will be analyzed by mass spectroscopy for a full understanding of the catalytic cycle. Yet, by using gaseous FA instead of TRI, an energy-intensive synthesis step for the preparation of starting material can be avoided, with the concurrent OME_n synthesis proceeding quickly with high yield and minimal amounts of by-products. In addition, product work-up is facile and moves OME_n production one step closer towards a sustainable OME_n synthesis starting from CO₂ and H₂.

Experimental and Method Section: In a typical experiment the catalyst ($OMe_3^+[X]^-$, 0.8 - 3.0 mol.%) was dissolved in OME_1 (2 - 5 mL; with or without addition of MeCN) and a cooler (-45 °C) was placed on top of the reaction flask. Gaseous FA was introduced into the solution at 25 - 30 °C under permanent stirring. After the FA-introduction was completed, the solution was stirred (typically for 30 min, in some cases also for 72 h), and NaOMe was added for quenching at 0 °C. The suspension was filtered and the obtained OME_n filtrate was analyzed via NMR spectroscopy. Further details are provided in ESI - Section 9.

Supporting Information: Full experimental details, procedures, weights, NMR spectra of the reactions, IR and Raman data are deposited. Details to the quantum chemical calculations are given together with crystallographic details.

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