On the oligomerization mechanism of Brønsted acid-catalyzed conversion of furans to diesel-range fuels

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Abstract

The conversion of biomass to fuels and chemicals is considered to be a promising alternative to petroleum-based conventional routes. The oligomerization of biomass-derived furans can yield an important precursor toward diesel fuel; yet, the underlying mechanism is not well-understood. This study investigates the furan oligomerization mechanism and kinetics via density functional theory and microkinetic modeling. The oligomerization proceeds in the presence of water and a Brønsted acid and requires an aldehyde and two furan molecules, each with at least one unprotected α -C. If only furans are present in the acidic, aqueous environment, the initial hydrolysis to produce the aldehyde limits the oligomerization rate. Two strategies to accelerate the oligomerization are proposed: furnishing the furans with electron-donating substituents or supplying a non-self-condensing aldehyde in the reaction mixture.

Keywords

Furans, Oligomerization, Diesel, DFT, Brønsted Acid Catalysis, Biomass

Introduction

Diminishing natural resources demand a change in the way we nourish our ever-growing need for fuels and chemicals by replacing conventional petroleum-based routes with sustainable ones. Out of the extensive pool of plausible strategies, biomass is an important renewable source, with furans being a promising intermediate platform. A recent example for the production of fuel from furans is the trimerization of 2-methylfuran (MF), a furfural derivative, to 5,5-bis(5-methyl-2-furyl)pentan-2-one, whose subsequent hydrodeoxygenation leads to high-quality diesel (Figure 1).^[1] When a Brønsted acid at 50 °C and palladium or platinum catalysts at 350 °C were used, the respective reactions, oligomerization and hydrodeoxygenation, proceeded with high yields.^[2-3] Corma and co-workers further exemplified the “oligomerization” of MF with a number of biomass-derived aldehydes and ketones; notably, aldehydes (e.g., pentanal) exhibited higher reaction rates than ketones (e.g., 2-pentanone).^[2] Besides the acid-catalyzed oligomerization, the polymerization of furans with oxidizing agents has been investigated.^[4-6] During this reaction, the furan rings do not open and the furan chain (polyfuran) is dehydrogenated. The carbon content of such long furan chains is beyond the relevant fuel-range.

Furan oligomerization is also important in the sustainable production of aromatics. Dauenhauer and co-workers have recently synthesized aromatics, such as para-xylene, toluene, and benzene, from furans and olefins in a two-step process in the Brønsted acidic zeolites HY and H-BEA. The first step is Diels-Alder cycloaddition between the furan and the olefin; the second is dehydration of the cycloadduct.^[7-9] The strong affinity of the more polar furans for the active site of HY leads to oligomeric byproducts

due to furan hydrolysis,^[9] since the reaction conditions resemble those in the trimerization of furans to diesel precursors.

Despite the importance of furans in biomass processing, their rich chemistry is still poorly understood. Specifically, the mechanism underlying the acid-catalyzed oligomerization reactions is unknown. It has been suggested that during oligomerization, one furan molecule first undergoes hydrolytic ring opening and then reacts with two closed-ring furan molecules, one at a time.^[2, 10] It is, however, not clear why certain furans, e.g., MF, form oligomers and polymers while others like 2,5-dimethylfuran (2,5-DMF) do not.^[11] The rate-determining step is also unknown. The goal of this study is to understand the reactions underlying the trimerization of furans. We first map out the mechanism and its energetics and then study the kinetics of self-trimerization of furan and of MF and the trimerization of MF with 5-methylfurfural. Moreover, we explain a number of experimental observations made in the literature, namely that 2,5-DMF -- in contrast to MF and furan -- does not trimerize; and that formyl groups, rather than keto groups, participate in the oligomerization. Finally, we discuss the implications of our study and strategies to accelerate or retard their production.

Methods

We perform density functional theory (DFT) calculations at the M062X/6-311+G(d,p) level,^[12] using Gaussian09 (Rev.A.2)^[13] with two closed-ring furan molecules and one hydrolyzed furan molecule in a conductor-like polarizable continuum water solvent model. The Brønsted proton is modeled with a Zundel H_5O_2^+ complex. All ground state compounds, i.e., reactants, intermediates and products, were connected with transition states, which were confirmed by integrating the intrinsic reaction coordinate. Cartesian coordinates of all transition states of the trimerization of MF can be found in Table S2 of the supplementary information (SI).

We develop a microkinetic model based on the mechanism and energetics obtained from DFT. By employing transition state theory, we convert forward and backward reaction barriers of each elementary step into the corresponding rate constants (Table S7). The differential rate expressions, shown in Table S3 and Table S6, were solved using Matlab.^[14]

Results

Oligomerization Mechanism

The hydrolysis of MF to produce 4-oxopentanal precedes the formation of the oligomer; the associated hydrolysis mechanism and energetics are depicted in Figure S1. The hydrolysis may proceed via initial protonation of the furanic α -C or β -C.^[15] Calculations, however, suggest that only the latter is active (Figure S2), as protonation of the β -C carbon requires 19 kcal/mol of free energy versus 27 kcal/mol for the protonation of the α -C, at 50 °C (typical experimental temperature^[2]). After the hydrolysis, an electrophilic substitution of the ring C5-H of an MF molecule by a 4-oxopentanal molecule protonated at the formyl O ensues; the associated mechanism and energy profile are shown in Figure 2 and Figure 3. The substitution proceeds through two transition states and thus follows $\text{S}_{\text{E}}1$ mechanism; the free energy barrier for the electrophilic attack (Figure 2, *Step 1*) is 11.9 kcal/mol, and that for the proton abstraction by a water molecule (acting as the base) is 12.4 kcal/mol (*Step 2*). Fast dehydration of the intermediate III (*Step 3*, $E_{\text{A}} = 12.5$ kcal/mol) results in the formation of a carbocation, which

electrophilically attacks a second MF molecule and substitutes its C5-H hydrogen. This electrophilic substitution, too, proceeds through two transition states, with free energy barriers of 10 and 10.7 kcal/mol for the electrophilic addition of the carbenium (*Step 4*) and the proton abstraction (*Step 5*), respectively. The same mechanism applies to the trimerization of furan, with similar energetics; in this case, however, the reaction can carry on to form a polymer (Table S4). In the entire mechanism, the step with the higher free energy barrier is the hydrolysis of furans.

Thus, according to this mechanism, furan can self-polymerize while MF can only self-trimerize in acidic, aqueous environments, and this is consistent with experimental observations.^[10] On the other hand, 2,5-DMF may only undergo hydrolysis to 2,5-hexanedione,^[11] since the methyl substituents on the α -carbons of the ring inhibit electrophilic substitution on account of not being good leaving groups (Figure S3).

Aldehydes are stronger electrophiles than ketones. Thus, under similar reaction conditions, significantly more oligomer forms when MF reacts with pentanal than with 2-pentanone.^[2] Similarly, the formyl group of 4-oxopentanal is more reactive than its keto group and the trimer associated with electrophilic attack from the formyl group forms in high purity.^[2] We also note that the lowest unoccupied molecular orbital of 4-oxopentanal is localized on the formyl group (Table 1). Thus, according to our calculations, electrophilic attack by the formyl group of 4-oxopentanal is somewhat favored over that by the keto group by 3.4 kcal/mol, and the corresponding intermediate is thermodynamically more stable by 8.3 kcal/mol, at 50 °C.

Microkinetic Modeling and Strategies for Trimerization Control:

In Figure 4, top panel, we show the network of reactions we considered in the microkinetic model for the oligomerization of MF in aqueous acidic medium (pH=2) at 50 °C. Below, we present the time-dependent concentration profiles obtained when initially pure MF (Figure 4, bottom left panel) or a 5:1 mixture of MF and 5-methylfurfural (Figure 4, bottom right panel) were present, to reproduce the experimental conditions used by Corma and co-workers.^[2]

The model reveals that the MF hydrolysis proceeds via initial protonation of the β -C, and that only the formyl group of 4-oxopentanal performs the hydroxyalkylation (Trimer A). The activity of the respective competing pathways—hydrolysis via initial protonation of the α -C or formation of *Trimer B* upon hydroxyalkylation with the keto group of 4-oxopentanal—is negligible (Figure 4, bottom left panel). The model predicts that the consumption of MF closely follows the production of the trimer, i.e., no intermediates accumulate except for a small amount of the Dimer (*III*). Sensitivity analysis reveals that the hydrolysis-initiating β -C protonation of MF limits the overall oligomerization rate (Figure S6). So, MF trimerization follows general acid catalysis, since its rate is determined by the initial proton transfer from the acid catalyst to the furan.

Based on the results presented above, several strategies could be proposed to increase the productivity of the process. Lower pH values and higher temperatures should accelerate the rate-limiting proton transfer. Alternatively, proton affinity calculations suggest that, because the initial protonation of the β -C of furan limits the rate of oligomerization, furans with electron-donating substituents (e.g. alkyl, phenyl, or alkoxy groups) at the α -position would undergo facile protonation at the β -C position, with the caveat that electrophilic substitution can only proceed^[15] so long as the furan is mono-substituted at the α -position or di-substituted with good leaving groups that do not participate in reactions that lead to byproducts (e.g., carbonyl and hydroxyl groups).^[16]

A conceptually different approach to increase the oligomerization rate would be to bypass the rate-limiting furan protonation by co-feeding an aldehyde that does not undergo self-aldol condensation, i.e., an aldehyde whose α -C is not coordinated to a hydrogen atom. To test this hypothesis, we extended the microkinetic model to include the reaction between 5-methylfurfural and MF (Figure 4, top and bottom right panels; associated reaction mechanism, elementary steps and energetics are given in Figure S4, Table S6 and Table S4, respectively). The concentration profiles show that the corresponding trimer (*Trimer C*, Figure 4) forms significantly faster than *Trimer A*. 5-methylfurfural is almost entirely converted to *Trimer C*, and a significant portion of MF is already consumed before *Trimer A* is produced. Accordingly, high selectivities to *Trimer C* can be achieved depending on the operating conditions and on the amount of 5-methylfurfural supplied. This observation is in agreement with experiments, run at a 5:1 molar ratio of MF to 5-methylfurfural, in which *Trimer C* was obtained with selectivity $S = 77 - 98\%$ for different acids.^[2]

Humins are furanic in nature and exhibit similar intramolecular linkages as the oligomers studied in this work. [17] Considering the structural features common to the furan oligomers shown above and humins, it is conceivable that the formation of humins during the acid-catalyzed sugar dehydration proceeds – in part – through similar reaction steps as those considered above. Consequently, humin formation, a key problem in the conversion of biomass derivatives to value-added products, could also be controlled with similar strategies proposed in this work. Future work is needed to explore all important pathways in humin formation.

Conclusions

In this work we elucidated the mechanism of the Brønsted acid-catalyzed trimerization of furans using density functional theory and microkinetic modeling. All reactants were embedded in an acidic, aqueous environment, which we modeled with a Zundel H_5O_2^+ complex in a dielectric continuum.

In acidic, aqueous media, self-trimerization of MF and self-polymerization of furan proceed through hydrolysis of the ring and subsequent ring electrophilic aromatic substitutions. Microkinetic modeling revealed that the initial hydrolysis (protonation at the C2 position) is the rate-limiting step of the trimerization and that no intermediates accumulate in the course of the reaction.

Out of the ever-growing inventory of biomass-derived furans, MF is particularly suitable for the trimerization and eventually diesel-range fuel because it possesses only one unprotected α -C. Accordingly, 2,5-DMF cannot oligomerize, while furan polymerizes since it has two unprotected α -C. Lower pH and higher T will increase the rate of oligomerization. Also, addition of an aldehyde that does not self-condensate, such as 5-methylfurfural, provides a new path that further accelerates the rate of growth of the carbon backbone. Our kinetic study supports this hypothesis by showing that, indeed, 5-methylfurfural (and not 4-oxopentanal) is preferentially used to assemble the trimer. An alternative strategy to accelerate the oligomerization is to furnish the furans with electron-donating substituents, such as alkyl, phenyl or alkoxy groups, at the α -C position to accelerate the proton transfer that limits the hydrolysis, as long as they do not activate side reactions. Furthermore, the furans must either be mono-substituted at the α -C or di-substituted with good leaving groups in order to allow the electrophilic substitution to proceed. Thus, rigorous control of the molecular composition of the reaction mixture is of utmost importance to avoid unwanted polymerization and possibly humin formation.

The operating conditions employed for the trimerization by Corma and co-workers ^[2] resemble those used in the conversion of furans to aromatics, ^[9] where unknown oligomers comprise, in large part, the unwanted side products: About half of MF and more than half of furan were consumed in oligomerization, while 2,5-DMF was almost completely converted to p-xylene. It is thus conceivable that some of the oligomers in ref. ^[9] are produced through a mechanism which requires an unprotected α -C to proceed, like the one presented in this work. An interesting strategy to prevent the unwanted oligomerization would therefore be to use furans with protecting substituents that can later be removed.

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Table 1: Electrophilic substitution on the C5 carbon of 2-methylfuran by either the formyl or the keto group of 4-oxopentanal. Shown are the free energy barriers (E_A) and free energies of reaction (ΔG_r) at 50 °C.

Reaction occurs on R ₁ / R ₂	formyl group CH ₃ / H	keto group H / CH ₃
E _A [kcal/mol]	+ 11.9	+ 15.3
ΔG _r [kcal/mol]	- 2.3	+ 6.0
UMO involved in reaction (Orbital energy [Hartree])	LUMO (0.00971)	LUMO+2 (0.01738)

Figure

Figure 1: The conversion of 2-methylfuran to high-quality diesel proceeds through a stable furan trimer intermediate.

Figure 2: Mechanism for the formation of 2-methylfuran trimer, 5,5-bis(5-methyl-2-furyl)pentan-2-one, in acidic environments. The reaction energetics for $R=CH_3$ and $R=H$ are depicted in Table S4. According to this mechanism 2,5-DMF cannot oligomerize.

Figure 3: Free energy (ΔG) profiles at 50 °C for the trimerization of two 2-methylfuran molecules and 4-oxopentanal, including solvent re-organization steps. “TS1–TS5” refer to “Step1 – Step5” of Figure 2. “TS-I – TS-V” refer to solvent re-organization steps during optimization. Numeric values can be found in Table S1.

Figure 4: Top panel: Reaction network considered in the microkinetic model. The network consists of hydrolysis of 2-methylfuran, via protonation either of the C2 or of the C3 carbon, oligomerization of 2-methylfuran either via the formyl or via the keto group of 4-oxopentanal (to form *Trimers A* and *B*, respectively), and oligomerization of 2-methylfuran in the presence of 5-methylfurfural (to form *Trimer C*). Bottom panels: concentration profiles at pH 2, 50 °C when initial concentration of 5-methylfurfural $c_{0, MFurf} = 0 \text{ mol/L}$ (left panel) and $c_{0, MFurf} = 0.2 \text{ mol/L}$ (right panel).