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Mechanistic study for the formation of polyoxymethylene dimethyl ethers promoted by sulfonic acid-functionalized ionic liquids

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ABSTRACT

Polyoxymethylene dimethyl ethers (DMM_n), which are ideal additives for diesel fuel, are mainly synthesized from the condensation of methanol (MeOH) or dimethoxymethane (DMM) with 1,3,5-trioxane (TOX) or paraformaldehyde (PF) promoted by different acid catalysts. However, up to date, few studies have been reported to examine the formation mechanism of DMM_n which is essential in understanding the reaction and valuable in designing improved catalysts. In this work, using the density functional theory (DFT) calculations combined with experiment studies, we evaluate the formation mechanism of DMM_n which is promoted by sulfonic acid-functionalized ionic liquids (SO_3H-FILs). Our calculated results indicate TOX and PF should dissociate into formaldehyde monomers firstly and then to react with MeOH or DMM. However, their decomposition process is different where the dissociation of TOX proceeds along a two-step mechanism while it follows a one-step mechanism for PF dissociation. As for the formation of DMM_n, the reaction proceeds along a hemiacetal-carbocation pathway when MeOH is selected as the capping group provider, while the reaction follows a carbocation pathway when DMM is chosen. The origination for the product distribution pattern has also been discussed in detail. The cations and anions of ionic liquids are found synergistically promote the condensation reaction by proton transfer and simultaneously stabilizing the formed intermediated and transition states. Moreover, all the processes related to the decomposition of TOX and PF and the condensation reaction are reversible.

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1. Introduction

Polyoxymethylene dimethyl ethers (DMM_n, generally $1 \leq n \leq 8$) are a series chain compounds with the formula $CH_3O(CH_2O)_nCH_3$ containing high oxygen contents (42–51%) and cetane numbers (CN). Especially, the CN of DMM_n with $n = 3$–8 is up to 76 or more and the oxygen contents is between 47% and 50%, making them be considered as the promising green additives to diesel fuel, which can lead to the improved thermal efficiency, and the significantly reduced emissions of particular materials, such as CO_x and NO_x. Therefore, the synthesis and application of DMM_n have attracted worldwide attentions [1–13]. Two type raw materials are required for the synthesis of DMM_n: one refers to a compound providing —CH_2O— group as a chain segment, such as 1,3,5-trioxane (TOX), paraformaldehyde (PF), or formaldehyde (FA), and the other is a compound which offers CH_3-capping group, such as methanol (MeOH), dimethoxymethane (DMM), or dimethyl ether (DME).

Both these two type compounds can be synthesized from MeOH which mainly produced from coal and natural gas and facing seriously overplus. Thus, the synthesis of DMM_n also promotes the transformation of MeOH into clean energy.

So far, many catalysts have been developed for the condensation reaction, such as liquid acids [1], solid superacid [2,3], ion exchange resin [4–10], molecular sieves [11,12], metal oxide [13] and so on. However, few catalysts are suitable for industrial application, so the exploration of effective and environmentally benign catalysts for the acetalization process needs to be solved urgently as oil resources are dwindling gradually. In recent years, our group have developed several sulfonic acid-functionalized ionic liquids (SO_3H-FILs) which are found very effective in promoting the condensation reaction [14,15]. The consecutive research found this catalyst possess many advantages, such as enhance the conversion of raw materials up to 90%, increase the selectivity for DMM_{3-8} up to 40% and so on, which suggest the condensation reaction catalyzed by SO_3H-FILs exhibiting promising application prospect.

For the formation of DMM_n, there are several key points we concerned: (1) do TOX and PF decompose firstly before they reacting with MeOH or DMM_n? (2) how does the chain length actually

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propagate? (3) do different capping group providers, such as MeOH and DMM, lead to distinct reaction pathways? (4) what roles do the catalysts indeed play in the reaction? However, to the best of our knowledge, the published articles and patents are concentrated on the synthesis of DMM$_n$, the development of catalysts [3,4,10], reaction kinetics [9,13,16,17], and chemical process design [18–22]. Few computational studies have been conducted to investigate the questions listed above to date at a molecular level for this important reaction regardless of which kind catalysts being used. In particular, employing experimental methods Zhao et al. [23] have found the growth of DMM$_n$ chain is carried out via addition FA one by one and the products distribution follow the Schulz–Flory law which restricts the increase of the selectivity to the desired products. However, the detailed reaction pathways are still unknown. Zheng et al. based on their experiment studies proposed DMM$_{n+1}$ are probably formed from the directly addition of protonated FA into C—O bond of DMM$_n$ [10]. However, the proposed mechanism has not been validated no matter by computational analysis or experimental methods. As for the possible form of TOX or PF to react with end-capping species, Burger et al. have proposed TOX may decompose into a linear trioxymethylene chain firstly and then this chain complex directly inserted into another DMM$_n$ leading to the formation of DMM$_{n+3}$, such as DMM$_4$, DMM$_7$ and so on. But they didn't observe the favorite formation of DMM$_4$ and DMM$_7$ in experiments [9,24].

To clarify the problems listed above, we have carried out a detailed density functional theory (DFT) study for the reactions of TOX/PF with MeOH and with DMM, as depicted in Scheme 1. Based on previous reports of our group [14], 1-(4-sulfonic acid)-butyl-3-methylimidazolium hydrogen sulfate [BsMim][HSO$_4$] are chosen as the catalysts. We expect the present results will provide new insights into the formation mechanism of DMM$_n$ and explain the previous experimental observations in some extent.

2. Computational and experimental details

2.1. Computational methods

All the DFT calculations were carried out with the Gaussian 09 software package [25]. The hybrid GGA functional B97D [26] which includes dispersion corrections combined with 6-31+G(d,p) [27–30] basis set was selected for the geometry optimization. All geometries were fully optimized without any symmetry constraints. The geometries for the transition states were located employing the synchronous transit-guided quasi-Newton (STQN) method [31] and Berny algorithm [32]. Vibrational frequency analysis was performed to confirm the nature (minima or first-order saddle points) of the stationary points at the same level. Zero-point energy corrections were carried out for all calculated energies. The intrinsic reaction coordinate (IRC) [33] was conducted in both directions (forward and reverse) from the transition states to the corresponding local minima to identify the minimum-energy paths. To take the entropy effects into account, the Gibbs free energies (ΔG) were used in the following discussion.

2.2. Experimental details

[BsMim][HSO$_4$] were prepared according to the similar procedure reported previously [34,35]. DMM$_3$ (99.9%, technical) was separated from DMM$_n$ mixtures.

For the decomposition of DMM$_3$, DMM$_3$ and [BsMim][HSO$_4$] catalyst with a mass ratio of 50:1 were charged into a 100 mL glass reactor. The reaction was performed with rapid agitation by magnetic stirrer at 30 °C and 0.1 MPa. The products were identified and quantitatively analyzed by gas chromatography (GC, Agilent 6890)

equipped with a flame ion-ization detector (FID) and a SE-54 capillary column (60 m × 0.25 mm × 0.25 μm). High purity nitrogen was used as the carrier gas. It is worth noting that, to avoid further process of the reaction, the ionic liquids have been separated from the sample before GC analysis. Firstly, acetic ether (2.0 g), internal standard (furanidine, 0.02 g), and small amounts CaO (which was used to neutralize any possible acids in the sample mixture) were put into a vial. Then the reaction sample (about 0.2 g) was rapidly transferred to the vial. Thus, ionic liquids were separated owing to its insolubility in acetic ether.

The unconverted FA is ascertained by titration method. Two drops of thymol phthalein indicator were added into the sodium sulfite solution (1 mol/L, 20.0 g) firstly, and then this solution was neutralized to colorless by sulphuric acid. Next, the reaction sample (1.0 g) was added into the obtained solution and shocked to blue. At the end, the content of FA can be determined by the titration of sulphuric acid (0.1 mol/L).

Molar distribution of every component was adopted to clearly show the content of DMM$_n$ yielded from the decomposition of DMM$_3$, which is defined as

$$m_d(n, t) = \frac{m_{DMM_n}/M_{DMM_n}}{m_{total}}$$

where m_{total} = the sum mass of all components which is set as 100 g, m_{DMMn} = the mass of DMM$_n$, M_{DMMn} = molar mass of DMM$_n$. The unit of molar distribution is mol/100 g. During the decomposition of DMM$_3$, the total mass of all components is a constant while the total mole amounts of DMM$_n$ keep varying. To clearly reflect the changes of the individual component, the total mass of DMM$_n$ was chosen as the denominator. It is worth noting that the molar distribution (mol/g) is not given as the complement to 100% while the total mass fraction (g/g) would be 100%.

3. Results and discussion

3.1. The decomposition of TOX and PF

Before analyzing the reaction mechanism, the chain segment provider TOX and PF dissociate or not with the assistance of SO$_3$H-FILs were firstly examined. This will be helpful to understand how DMM$_n$ chains increase in the following steps.

3.1.1. TOX decomposition

As can be seen in Fig. 1, beginning with the SO$_3$H-FIL + TOX, a two-body complex **IM1** is firstly formed via hydrogen-bonding interaction between H atom of SO$_3$H moiety and one O atom of TOX. Subsequently, **IM1** can go through **TS$_{1-2}$** to open the six-membered ring and produce a linear trioxymethylene chain complex where the carbocation side is stabilized by the O atom of HSO$_4^-$ anion (see **IM2**). This process is carried out via the migration of H atom of SO$_3$H to O atom of TOX making one C—O bond of TOX be broken. 20.22 kcal mol^{-1} is required to conquer the energy barrier. It is worth to note that the geometry of trioxymethylene chain is very similar to that of hemiacetal. And then the transferred hydrogen atom goes back to SO$_3$H-FIL making the decomposition of TOX, i.e., the formation of monomeric FA, as the large C—O bond distances 2.072 and 1.968 Å have been illustrated in **IM4**. The saddle point about this step is **TS$_{3-4}$** with a barrier of 13.45 kcal mol^{-1}. The separation of monomeric FA from SO$_3$H-FIL, which is exothermic by 15.18 kcal mol^{-1}, completes the whole process. According to the results discussed above, it is obviously found that the decomposition of TOX into FA monomers occurs via two steps: (i) the protonation of TOX by SO$_3$H-FILs resulting in the six-membered ring opening and the formation of a linear trioxymethylene chain complex, (ii) the decomposition of the chain complex to produce