Theoretical Studies of the Hydrogen Abstraction from Poly(oxymethylene) Dimethyl Ethers by O₂ in Relation with Cetane Number Data

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Supporting Information

ABSTRACT: Poly(oxymethylene) dimethyl ethers (PODMEₙ, n = 2–6) are novel oxygenated compounds that can be used as promising candidates for new-generation fuels because of their excellent combustion performance. The oxidation of PODMEₙ (n = 2–6) is essential for the understanding of the combustion process. It is necessary to study the relationship between kinetic parameters and cetane number (CN) of PODMEₙ (n = 2–6). In order to predict initiation step rate constants for the oxidation of PODMEₙ (n = 2–6), quantum mechanical calculations are performed using M06-2X/6-311G(d,p) and B3LYP/6-311G(d,p) methods. Structural, energetic, thermodynamics, and kinetics of the automatic ignition process are assessed. The kinetic model based on the conventional transition state theory is used to calculate the initiation step reaction rate constants at 1000 K. In both M06-2X/6-311G(d,p) and B3LYP/6-311G(d,p) methods, the calculated rate constants of the hydrogen abstraction process have an excellent correlation with the experimental CN of PODMEₙ (n = 2–6). Our methodology presented here can be used to simulate chemical kinetics for other fuel additives.

1. INTRODUCTION

Cetane number (CN) is an important index to evaluate the ignition performance of diesel, whose value has important influence on diesel engine cold start, emission performance, and combustion noise.⁵⁻⁷ The ignition quality of the diesel fuel is closely related to the chemical composition.⁴⁻⁶ Oxygenated compounds (molecules which contain oxygen in their structure) can be used as additives or substituents to diesel fuels, which could greatly reduce nitrogen oxides (NOₓ) and particulate pollutants in tail gas and improve the combustion performance of diesel fuels.⁶⁻⁸ As a new type of diesel additive, poly(oxymethylene) dimethyl ethers (PODMEₙ) can significantly improve the combustion performance of diesel fuels, effectively improve the thermal efficiency, and greatly reduce NOₓ and soot emissions.⁹⁻¹² In particular, the average CN of PODMEₙ (CH₃O(CH₂O)ₙCH₃ with 2 ≤ n ≤ 6) is more than 76, the oxygen content is up to 47–50%, the boiling point is more than 160 °C, and all the indices fall within the range of diesel indices.⁹⁻¹² Furthermore, PODMEₙ have a good miscibility with an ordinary diesel fuel and are an environmentally friendly diesel blend components with great application prospects.¹¹⁻¹³ The combustion and emission characteristics of the (diesel + PODME₃₋₄) mixtures with the PODME₃₋₄ volume blending ratios 10 and 20% have been investigated in a light-duty direct injection diesel engine.¹⁴ The results show that PODME₃₋₄ can significantly improve the engine efficiency and reduce soot emissions.¹⁴ The effects of (diesel + PODME₃₋₆) mixtures on the combustion and emission characteristics of a heavy-duty diesel engine have been studied with the PODME₃₋₆ volume blending ratios 15 and 25%.¹⁵ Compared with diesel without PODME₃₋₆, the soot emissions could be reduced by 88 and 95% with the addition of 15 and 25% PODME₃₋₆ respectively.¹⁵ Therefore, PODMEₙ (n = 2–6) have potential to be an environmentally friendly additive that significantly reduces soot formation in diesel engines.

Received: July 31, 2019
Accepted: October 24, 2019
Published: November 6, 2019
diezel engines. The general trend of CN value increasing with the chain length is still valid for PODMEₙ (n = 2−6). 16,22

To understand the effect of CN improver on diesel combustion, it is important to understand the initiation step that the CN improver creates free radicals qualitatively. 16,21 Therefore, a great deal of research has been done on this topic. 17−21 In general, for the hydrogen abstraction reactions between organic compounds and oxygen, shell opening oxygen induces the formation of reactive free radicals, followed by branched chain oxidation. 17−21 The reactive free radicals produced in the initiation step are generated by the reaction of fuel (RH) with oxygen. 6,17,22 The mechanism of hydrogen abstraction reactions is simple, which can be illustrated clearly by quantum chemistry theory. 20,21 Numerous related computational studies have been carried out in the literature ranging from the Hartree–Fock (HF) theory to hybrid density functional theory (DFT), such as the popular B3LYP, BH&HLYP, M06-2X, and M08-HX methods. 16,16,22 Kalia-guine et al. had studied the theoretical kinetic on a few simple compounds, such as n-paraffins (C₂−C₆), primary linear alcohols (C₂−CS), dimethyl ether, diethylether, and methylal. 6−8 The results were consistent with the hypothesis that the rate constants in the initiation step of the autoignition process of compounds being studied were correlated with the experimental CN of these oxygenates. 6−8

To our knowledge, theoretical kinetic data of the auto-ignition process of the PODMEₙ and its correlation with the corresponding experimental CN data have not been reported in the literature. Hence, the objective of this work is to study the theoretical kinetic data of the autoignition process of PODMEₙ (n = 2−6) and to study the relationship between quantum calculation results and the experimental CN of these compounds.

2. RESULTS AND DISCUSSION

2.1. Structures and Energetics. In the combustion or general oxidation of RH, a bimolecular gas-phase reaction is considered as the initiation step, given as follows: 16,21

\[ \text{RH} + \text{O}_2 \rightarrow \text{R} \cdots \text{H} \cdots \text{O}_2 \rightarrow \text{R}^* + \text{HO}_2^* \] (1)

In this reaction, an oxygen molecule reacting by H-abstraction with the initial organic compounds leads to the formation of the radicals R* and HO₂* via a molecular transition state (TS) [R···H···O₂].

The optimal geometric structures of reactants, products, and TSs that connect reactants and products are searched. The geometrical optimizations of PODMEₙ (n = 2−6) molecules show the distorted helix structure and minimum energy, similar to the gg-helix of polyoxymethylene. 23,24 The geometry optimized at the B3LYP/6-311G(d,p) level of theory is very similar to the structure obtained with M06-2X/6-311G(d,p).

**Figure 1** shows the structure of PODME₅ using the M06-2X/6-311G(d,p) method as an illustration. The Mulliken charges of atoms of PODME₅ are shown in **Table 1**. Although some hydrogen atoms bonded to the same carbon atom are not rigorously equivalent to each other, the energy differences between the TSs of the H-abstraction reactions are <0.2 kcal/mol, which could be ignored. Hence, it is reasonable to treat them as identical. For example, according to the positions of hydrogen atoms of PODME₉, these hydrogen atoms can be divided into four groups. For comprehensive study of the reaction mechanism, all O₂-attack possibilities have been taken into account in **Table 2** based on the different hydrogen sites.

**Table 1. Mulliken Charges of Atoms of PODME₅ Using B3LYP and M06-2X Methods**

| label | atom | B3LYP | M06-2X |
|-------|------|-------|--------|
| 1     | C    | −0.124| −0.197 |
| 2     | H    | 0.116 | 0.140  |
| 3     | H    | 0.109 | 0.137  |
| 4     | H    | 0.091 | 0.119  |
| 5     | O    | −0.357| −0.368 |
| 6     | C    | 0.144 | 0.084  |
| 7     | H    | 0.117 | 0.150  |
| 8     | H    | 0.095 | 0.130  |
| 9     | O    | −0.374| −0.380 |
| 10    | C    | 0.137 | 0.073  |
| 11    | H    | 0.116 | 0.151  |
| 12    | H    | 0.116 | 0.152  |
| 13    | O    | −0.370| −0.376 |
| 14    | C    | 0.136 | 0.072  |
| 15    | H    | 0.115 | 0.150  |
| 16    | H    | 0.115 | 0.150  |
| 17    | O    | −0.370| −0.376 |
| 18    | C    | 0.137 | 0.073  |
| 19    | H    | 0.116 | 0.152  |
| 20    | H    | 0.116 | 0.151  |
| 21    | O    | −0.374| −0.380 |
| 22    | C    | 0.144 | 0.084  |
| 23    | H    | 0.095 | 0.130  |
| 24    | H    | 0.117 | 0.150  |
| 25    | O    | −0.357| −0.368 |
| 26    | C    | −0.124| −0.197 |
| 27    | H    | 0.116 | 0.140  |
| 28    | H    | 0.109 | 0.137  |
| 29    | H    | 0.091 | 0.119  |
Table 2. Possible Reaction Pathways of H-Abstraction of PODME₂ₙ (n = 2–6) by O₂

| systems | possible O₂-attack pathways |
|---------|----------------------------|
| PODME₂ | CH₂O(CH₂O)₂CH₃ + O₂ → CH₂O(CH₂O)₂CH₂ + HO₂ |
|  | CH₂O(CH₂O)₃CH₃ + O₂ → CH₂O(CH₂O)₂CH₂ + HO₂ |
| PODME₃ | CH₂O(CH₂O)₄CH₃ + O₂ → CH₂O(CH₂O)₃CH₂ + HO₂ |
|  | CH₂O(CH₂O)₅CH₃ + O₂ → CH₂O(CH₂O)₄CH₂ + HO₂ |
| PODME₄ | CH₂O(CH₂O)₆CH₃ + O₂ → CH₂O(CH₂O)₅CH₂ + HO₂ |
|  | CH₂O(CH₂O)₇CH₃ + O₂ → CH₂O(CH₂O)₆CH₂ + HO₂ |
| PODME₅ | CH₂O(CH₂O)₈CH₃ + O₂ → CH₂O(CH₂O)₇CH₂ + HO₂ |
|  | CH₂O(CH₂O)₉CH₃ + O₂ → CH₂O(CH₂O)₈CH₂ + HO₂ |

Due to the TSs of the combustion reaction of PODME₂ₙ (n = 2–6) molecules show similar structural characteristics at the corresponding H-abstraction position, there is just showing the molecular chain, the angles of C−H bond lengths (Å) in this work. Additionally, with an increase in the steric hindrance with H-abstraction position moving to the middle of the molecular chain, the angles of C−H−O increase in the order R₄a (126.5°/121.8°) < R₄b (141.7°/130.2°) < R₄c (148.9°/143.8°) ≈ R₄d (148.8°/143.7°) for B3LYP/M06-2X.

The angles of H−O−O are around 109° for both B3LYP and M06-2X. These are the features of H-abstraction reactions from O₂. Notably, with the exception of the H-abstraction from the methyl group and methylene group closed-end position, such as R₂b, R₃b, R₄b, and R₅b, H-abstraction from the methylene groups contained in the five molecules shows almost the same activation energy and TS structures.

As shown in Table S1, the reactants are almost as stable as the products by about 14.9−17.6 and 20.8−25.3 kcal/mol at B3LYP and M06-2X levels, respectively. Overall, the difference between the total energy of the products and their corresponding TS is smaller at the B3LYP level. In contrast, the total energy of products is about 0.4−6.4 kcal/mol below their corresponding TS at the M06-2X level. The activation energies for H-abstraction reactions of oxygen with PODME₂ₙ (n = 2–6), denoted as R₁−R₅ (a−d), are reported in Table 3. The relative energies ΔEᵢ and ΔEᵢ represent the calculated value of activation barrier between the reactants and the TS at B3LYP and M06-2X levels, respectively. It is concluded that the B3LYP functional has lower activation barrier than M06-2X with the same H-abstraction processes. This may be the B3LYP underestimate the activation barrier on account of self-interaction and delocalization errors. It can also be observed from Table 3 that the activation energy of the hydrogen atoms at each end of the chain is higher than that of the other hydrogen atoms in the molecular chain. For almost all reaction pathways of PODME₂ₙ (n = 2–6), H-abstraction is more likely to occur on methylene hydrogen than on methyl hydrogen. The Mulliken population analysis is also used to confirm this observation. The net charge of an atom in a molecule gives a rough idea of the electrostatic force between hydrogen and carbon atoms. Table 1 shows the Mulliken population analysis of atomic net charges of PODME₂ₙ using B3LYP and M06-2X methods. In PODME₂ₙ, because the electrophilic oxygen atoms decrease the electron density on carbon atoms, these carbon atoms of the methyl group and methylene group are negatively charged and positively charged, respectively. As a result, the C−H bonds of the methyl group have stronger and more attractive global charge than that of the methylene group.

2.2. Quantitative Study: Kinetic Modeling and Predicting CNs. The rate constant calculation for the bimolecular reactions of the autoignition process is implemented within formalism of the TS theory (TST). All the energy parameters of the reactants and the TS are shown in Table 3. The rate constant is calculated at 1000 K, which is used to simulate the temperature in the combustion chamber of the diesel engine. Consequently, the rate constant for these initiation steps kₜₛₜₛ(T) is computed using conventional TST24,46 in the following

\[ k_{i,T} = k_0 \exp(-\Delta G_{i,T}^0/RT) \]

where \( k_0 \) is the transmission coefficient of the corrected tunneling effect, \( k_0 \) is the Boltzmann constant, \( h \) is the Planck constants, \( R \) is the gas constant, and \( \Delta G_{i,T}^0 \) is the standard state Gibbs free energy of activation at temperature \( T \) and pressure \( P_0 = 1 \text{ atm} \). In this work, \( \Delta G_{i,T}^0 \) has been replaced by \( \Delta E \) in the calculation process of \( k_{i,T} \). Tunneling effects may be described quantitatively as the Wigner correction factor26,27
where $\nu^\ddagger$ (cm$^{-1}$) is the magnitude of the imaginary frequency of the TST. However, the tunneling effect has little effect at high temperature, such as 1000 K. Furthermore, the imaginary frequencies of all reactions studied here are exactly similar, and the correction of the tunneling effect has no significant effect on the observed relative reactivity. Hence, it makes sense to set $\kappa \approx 1$. The results of H-abstraction reactions are given in Table 4. It clearly shows that the order of the rate constants of these reactions (R1–R5) is the same in both B3LYP and M06-2X methods. Hence, the rate constants of H-abstraction reactions with PODME$_n$ ($n = 2–6$) are in accordance with the order PODME$_2 < PODME_3 < PODME_4 < PODME_5 < PODME_6$, which is well correlated with the experimental CN of these pure oxygenated compounds.$^9$–$^{12}$

Figure 2. Optimized TS structures in PODME$_5 + \text{O}_2$ at the B3LYP level of theory. (a) R4a; (b) R4b; (c) R4c; (d) R4d.
Results of Table 4 also indicate that the H-abstraction by O$_2$ from the middle methylene of PODME$_n$ ($n=2-6$) are the dominant paths among all reaction pathways attributed to its lowest barrier height. The additive group contribution approach is used to calculate the global rate constant, which includes the contribution of all H-abstract reactions for PODME$_n$ ($n=2-6$). The global rate constant of the additive rule is expressed as:

$$k_{\text{global}}(T) = \sum m_i k_{i,TST}$$  \hspace{1cm} (4)$$

where $m_i$ is the number of hydrogen atoms with the same chemical environment in PODME$_n$ ($n=2-6$) and $k_{i,TST}$ is the individual rate constant computed for each category of H-abstraction. The computed total rate constants $k_{\text{global}}$ and their logarithmic form log($k_{\text{global}}$) for PODME$_n$ ($n=2-6$) combustion reactions (R1−R5) are reported in Table 5. It is
Table 3. TS Barriers (in kcal/mol) for Hydrogen Abstraction Reactions

| reaction | transition state | $\Delta E_{t}$ | $\Delta E_{a}$ |
|----------|------------------|----------------|----------------|
| R1a      | $[\text{CH}_3\text{O}($CH$_2$O)$_2$CH$_2$($H$--$O$)$_2]$ | 17.35 | 25.03 |
| R1b      | $[\text{CH}_3\text{OCH}_2\text{OCH}--($H$--$O$)$_2$]$ | 15.44 | 21.57 |
| R2a      | $[\text{CH}_3\text{O}($CH$_2$O)$_2$CH$_2$($H$--$O$)$_2]$ | 17.42 | 25.09 |
| R2b      | $[\text{CH}_3\text{O}($CH$_2$O)$_2$CH$_2$($H$--$O$)$_2$]$ | 15.63 | 23.33 |
| R2c      | $[\text{CH}_3\text{OCH}_2\text{OCH}--($H$--$O$)$_2$]$ | 14.93 | 20.88 |
| R3a      | $[\text{CH}_3\text{O}($CH$_2$O)$_2$CH$_2$($H$--$O$)$_2]$ | 17.52 | 25.20 |
| R3b      | $[\text{CH}_3\text{O}($CH$_2$O)$_2$CH$_2$($H$--$O$)$_2$]$ | 15.82 | 23.56 |
| R3c      | $[\text{CH}_3\text{O}($CH$_2$O)$_2$CH$_2$($H$--$O$)$_2$]$ | 15.06 | 20.84 |
| R4a      | $[\text{CH}_3\text{O}($CH$_2$O)$_2$CH$_2$($H$--$O$)$_2$]$ | 17.54 | 25.18 |
| R4b      | $[\text{CH}_3\text{O}($CH$_2$O)$_2$CH$_2$($H$--$O$)$_2$]$ | 15.83 | 23.64 |
| R4c      | $[\text{CH}_3\text{O}($CH$_2$O)$_2$CH$_2$($H$--$O$)$_2$]$ | 15.07 | 20.83 |
| R4d      | $[\text{CH}_3\text{O}($CH$_2$O)$_2$CH$_2$($H$--$O$)$_2$]$ | 15.10 | 20.83 |
| R5a      | $[\text{CH}_3\text{O}($CH$_2$O)$_2$CH$_2$($H$--$O$)$_2$]$ | 17.58 | 25.24 |
| R5b      | $[\text{CH}_3\text{O}($CH$_2$O)$_2$CH$_2$($H$--$O$)$_2$]$ | 15.88 | 23.59 |
| R5c      | $[\text{CH}_3\text{O}($CH$_2$O)$_2$CH$_2$($H$--$O$)$_2$]$ | 15.05 | 20.90 |
| R5d      | $[O($CH$_2$O)$_2$CH$_2$]$ | 15.12 | 20.84 |

Table 4. Computed ($m \times k_{TST}$) Rate Constants in cm$^3$/mol/s for the Bimolecular Reaction Pathways (R1–R5) at 1000 K$^*$$^a$

| reaction | $m \times k_{TST}$ |
|----------|--------------------|
| R1a (m = 6) | $1.79 \times 10^6$ | $4.23 \times 10^{-1}$ |
| R1b (m = 4) | $2.99 \times 10^6$ | $0.98 \times 10^2$ |
| R2a (m = 6) | $1.59 \times 10^6$ | $3.84 \times 10^1$ |
| R2b (m = 4) | $2.18 \times 10^6$ | $4.95$ |
| R2c (m = 2) | $3.42 \times 10^5$ | $1.57 \times 10^2$ |
| R3a (m = 6) | $1.34 \times 10^5$ | $3.20 \times 10^1$ |
| R3b (m = 4) | $1.58 \times 10^5$ | $3.37$ |
| R3c (m = 4) | $5.71 \times 10^4$ | $3.35 \times 10^2$ |
| R4a (m = 6) | $1.30 \times 10^4$ | $3.29 \times 10^1$ |
| R4b (m = 4) | $1.56 \times 10^4$ | $2.96$ |
| R4c (m = 4) | $5.55 \times 10^3$ | $3.38 \times 10^2$ |
| R4d (m = 2) | $2.65 \times 10^3$ | $1.69 \times 10^2$ |
| R5a (m = 6) | $1.22 \times 10^3$ | $2.99 \times 10^1$ |
| R5b (m = 4) | $1.43 \times 10^3$ | $3.24$ |
| R5c (m = 4) | $5.74 \times 10^2$ | $3.02 \times 10^2$ |
| R5d (m = 4) | $5.14 \times 10^2$ | $3.34 \times 10^2$ |

$a$m is the number of hydrogen atoms with the same chemical environment in PODME$_n$ ($n = 2–6$).

Table 5. Global Rate Constants Calculated at 1000 K with B3LYP and M06-2X, with $k_{global}(T) = \sum m k_{m,TST}$

| systems | B3LYP | M06-2X | CN$_{exp}$ |
|---------|-------|--------|-----------|
| PODME$_3$ | 5.60 | 1.99 | 63 |
| PODME$_4$ | 6.76 | 2.21 | 78 |
| PODME$_5$ | 6.87 | 2.53 | 90 |
| PODME$_6$ | 7.00 | 2.71 | 100 |
| PODME$_6$ | 7.09 | 2.81 | 104 |

There is a significant positive linear correlation between the log($k_{global}$) calculated at 1000 K for reactions (R1–R5) and the reported CN values for the corresponding oxygenated compounds.9–12 The linear regression function based on the least-squares method is used and expressed at B3LYP and M06-2X by eqs 5 and 6, respectively:

$$\text{CN}_{cal} = 72.43 \log k_{global} - 408.74$$

$$\text{CN}_{cal} = 48.74 \log k_{global} - 32.37$$

In Figure 4, the calculated results are compared with the experimental CN data for each oxygenated compound in B3LYP and M06-2X methods. It is clear from Figure 4 that the calculated results are in good agreement with the experimental results for both examined cases. The standard deviation values in B3LYP and M06-2X methods ($\sigma_{CN} = \left( \frac{1}{N} \sum_{i=1}^{N} (\text{CN}_{cal} - \text{CN}_{exp})^2 \right)^{1/2}$, where N is the number of experimental data) are 0.80 and 0.67, respectively. The average relative deviation values in B3LYP and M06-2X methods ($\delta_{CN} = \frac{1}{N} \sum_{i=1}^{N} |\text{CN}_{cal} - \text{CN}_{exp}| / \text{CN}_{exp}$, where N is the number of experimental data) are 1.91 and 1.58%, respectively. Both correlations exhibit a higher CN value with PODME$_6$ than the reported CN value. It is possible that there is a negative deviation in the experimental value with PODME$_6$.

3. CONCLUSIONS

The oxygenated PODME$_n$ ($n = 2–6$) are attractive as clean diesel fuel or fuel additive. In this work, the theoretical kinetic data of the autoignition process of the PODME$_n$ in their helix configuration are calculated using conventional TST with B3LYP/6-311G(d,p) and M06-2X/6-311G(d,p) methods at 1000 K. Our study shows that the TSs of the combustion reaction of PODME$_n$ ($n = 2–6$) molecules show similar structural characteristics at the corresponding H-abstraction position. The B3LYP functional has lower activation barrier than M06-2X. For almost all H-abstraction pathways of PODME$_n$ ($n = 2–6$), the activation energy decreases as the H-abstraction position moves toward the middle of the molecular chain, H-abstraction occurs preferentially on the hydrogen of the methylene closed center rather than on the closed-end position. Hydrogen bonds are formed between the O atom of O$_2$ and H atom of methylene or methyl hydrogen. These hydrogen bonds could stabilize the TS structures. The linear relationship between the rate constant of the autoignition process of pure compound and the experimental CN data is established. Our calculated rate constants are in good agreement with experimental CN data. It is indicated that the calculation is reliable, and a relationship between kinetics and CN is established. The methodology presented here can be used to generate theoretical kinetic data for other fuel additives.

4. COMPUTATIONAL METHODS

Large varieties of computational methods indicate that the HF methods have been known to overestimate barrier heights, and pure DFT methods tend to underestimate the energy barrier.22,26,29–31 Hybrid DFT methods perform better for the computation of activation barriers than the pure DFT because of variation of the exact HF exchange energy term.22,52,53 In particular, B3LYP is one of the most popular...
determining the bimolecular rate constants of all reactions were performed using the hybrid DFT methods B3LYP and M06-2X. The present study provides new insights into the autoignition process of PODME
t (n = 2–6).

All the electronic structure calculations were performed using the Gaussian 16 software package. Calculation results of the geometrical optimizations and harmonic vibrational frequency for reactants, TSs, and products were performed with the hybrid DFT of B3LYP37–39 and M06-2X40 coupled with the 6-311G(d,p) basis set. All TSs were obtained by using the routine TS (Berry) method41,42. On the basis of the TST, the bimolecular rate constants of all reactions were calculated by using parameters and energy barriers obtained by the B3LYP and M06-2X methods without being scaled by the factor anymore. All the TS structures were confirmed by only one imaginary frequency, and intrinsic reaction coordinate calculations were also carried out to verify that the TS connects the corresponding reactants and products. The molecular oxygen O2 participated in the reaction in the form of ground triplet state, and the HO2 radical and R radical were considered as doublet states. The ZPE and thermal correction values were used for the evaluation of the reaction activation energies at 1000 K, which represented the operating temperature of diesel engine during the combustion process.4–6,16. The kinetic model for combustion reactions of PODME
t (n = 2–6) based on the conventional TST was used to calculate the rate constants at 1000 K.

### ASSOCIATED CONTENT

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b02424.

Calculated total energies (in hartrees) for reactants, TSs, and products included in combustion initiation reactions of PODME
t (n = 2–6) (PDF)

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**Notes**

The authors declare no competing financial interest.

### ACKNOWLEDGMENTS

We acknowledge the National Natural Science Foundation of China (nos. 21890763, 21776300, and 21576285), China Petrochemical Corporation (no. ZX20180062), Natural Science Foundation of Inner Mongolia (no. 2017BS0202), Program for Young Talents of Science and Technology in Universities of Inner Mongolia Autonomous Region (no. KYKT-18-B23), Teaching Reform Research Project of Ordes Institute of Technology (no. 20180217), and Scientific Research Project of Ordes Institute of Technology (nos. KYZD2017002 and KYYB2019006).

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