Study on chemical kinetic mechanisms of Polyoxymethylene Dimethyl Ethers (PODE\textsubscript{n})

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Abstract. Based on the latest detailed mechanism of Dimethoxymethane (DMM), a new chemical kinetic mechanism model of Polyoxymethylene Dimethyl Ethers (PODE\textsubscript{n}) with high degree of polymerization was preliminarily developed by extending reaction classes of DMM to PODE\textsubscript{3} with the same rate coefficient criterion. Compared with the existing PODE\textsubscript{n} model and experimental data, it was observed that the model of He could forecast the experimental data of PODE\textsubscript{3} accurately, but the prediction ability of the underlying DMM mechanism was poor. The model developed in this paper could forecast DMM experimental data accurately but could not forecast the experimental data of PODE\textsubscript{3} accurately. The same reaction classes of PODE\textsubscript{n} with different degree of polymerization did not have the same rate coefficient criterion.

1. Introduction

Diesel engines were widely used due to its high thermal efficiency and excellent power performance. In the future, the demand for diesel oil will be expanded and the emission regulations will be more stringent. Diesel alternative fuels are urgently needed to expand fuel supply and reduce pollutant emissions. Oxygenated alternative fuels, including alcohols, esters and ethers, have been widely used in internal combustion engines\cite{1,2}. Polyoxymethylene Dimethyl Ethers (PODE\textsubscript{n}) represent the mixture of ethers with the chemical formula of CH\textsubscript{3}O(CH\textsubscript{2}O)\textsubscript{n}CH\textsubscript{3}, where \( n \) (the degree of polymerization) is the number of CH\textsubscript{2}O group and usually ranges from 1 to 8. When \( n=1 \), it represents Dimethoxymethane (DMM). PODE\textsubscript{n} are generally synthesized from methanol with lower cost than hydrocarbons, which can greatly alleviate the problem of overcapacity of coal-based chemicals in China\cite{3}. Compared with traditional diesel alternative fuels, PODE\textsubscript{n} have high cetane number and high oxygen content (near 50%), and are used to improve the ignitability and combustion characteristics and reduce soot emissions\cite{1,4,5}.

The development of detailed chemical kinetics model is indispensable for understanding the basic combustion process and controlling the combustion process of internal combustion engine. At present, there are few studies on the chemical kinetics of PODE\textsubscript{n}, and most of them were focused on PODE\textsubscript{1}(DMM). Recently, a number of DMM chemical kinetics models with theoretical results of accurate rate constants were developed, and have been widely validated in jet stirred reactor (JSR), shock tube (ST) and rapid compression machine (RCM)\cite{6-9}. Sun\cite{10} constructed the first high temperature mechanism model of PODE\textsubscript{3} by analogizing the reaction mechanism of DMM and dimethyl ether (DME), and the model was verified by laminar flame combustion rate and species concentration distribution of premixed flame. He\cite{11} analogized the kinetic mechanism of DMM to PODE\textsubscript{2} and PODE\textsubscript{3}, and a detailed chemical kinetics model of PODE\textsubscript{3} covering the range of medium
and low temperature was developed (containing 225 components and 1082 reactions, named He model in this paper), and the model was validated on RCM and HCCI engines.

It can be observed that the kinetics models of PODE$_n$ with high degree of polymerization were dependent on the accuracy of the underlying DMM mechanism. The existing chemical kinetic mechanism models of PODE$_2$ and PODE$_3$ were lack of accuracy because the accuracy of the underlying DMM mechanism was not studied and the prediction ability of DMM mechanism was poor. In this paper, the kinetics model of PODE$_3$ was preliminarily constructed based on the reliable detailed mechanism of DMM, the effects of the mechanism difference of DMM on the mechanism of PODE$_n$ with high degree of polymerization were studied by comparing with the existing models and experimental data in the literature.

2. Construction of kinetics model

For PODE$_n$ with high degree of polymerization, it is difficult to calculate its elementary reaction rate constants theoretically due to the large number of atoms. Therefore, the rate constants of macromolecule elementary reactions are usually estimated by analogy from small chemically similar molecules, and then the complete chemical reaction mechanism is established.

The researches of Sun and He observed that it was feasible to develop PODE$_2$–$3$ mechanism based on DMM mechanism by hierarchical construction. Vermeire studied the potential energy surface of peroxides during low temperature oxidation of DMM at CBS-QB3 level, and thermodynamic data and elementary reaction rate constants of most species were derived. Jacobs[6] and Kopp[9] studied the kinetics and thermochemistry of some important reactions in the oxidation process of DMM by the methods of ab initio (CCSD(T)/aug-cc-pV(D+T)Z//B2PLYPD3BJ/6-311++g(d,p)) and statistical mechanics, and a detailed kinetics model of DMM containing 6 high-temperature reaction classes and 15 low-temperature reaction classes was developed by integrating the researches of Vermeire. This model (named Jacobs model in this paper) could forecast the experimental data of ST, RCM, JSR accurately. As shown in Figures 1 and 2, Jacobs model is an more accurate DMM model at present.

Based on He model, the core mechanism of C1–C4 small molecule was unchanged, but the mechanism of DMM was replaced by that of Jacobs model. At the same time, based on the concept of chemical similarity, 21 DMM reaction classes in Jacobs model were analogized to the mechanisms of PODE$_2$ and PODE$_3$. Some important reaction classes of this model were shown in Table 1, in which the symbolic definitions were similar to those of conventional alkanes. R and Ṙ represented the chemical groups of C$_n$H$_{2n+1}$O$_x$ and Q represented the chemical groups of C$_n$H$_{2n}$O$_x$. However, unlike conventional alkanes, there was not any reaction class of alkenes formation due to the lack of C-C bonds in PODE$_n$.

![Figure 1](image)

**Figure 1.** Comparison of ignition delay time of DMM under different chemical equivalence ratio and air dilution conditions. The solid point represented the experimental data in high-pressure shock tube of Jacobs, the solid line represented the predicted value of the model developed in this paper, the dotted line represented the predicted value of He model.
Figure 2. Comparison of main species concentration during DMM oxidation process under different chemical equivalence ratios. The solid point represented the JSR data measured by Vermeire, the initial concentration of DMM remained at 1%, the solid line represented the predicted value of the model developed in this paper, the dotted line represented the predicted value of He model. The analogy methods of He were adopted in the processes of analogy and the same rate coefficient criterion was used for the elementary reactions of same reaction class. For example, reaction classes 4 and 5 were the $\beta$-scission reactions of dehydrogenation radicals. Dehydrogenation radicals would be reacted with oxygen or consumed by $\beta$-scission directly, the competitive relationship between the two methods had a great influence on the overall reactivity of the fuel. As mentioned above, Kopp showed the theoretical rate constants of the $\beta$-scission reactions in DMM by means of high-precision quantum mechanics. The two main processes are as follows:

\[
\text{(1)} \quad \text{O} = \text{O} + \text{O}
\]

\[
\text{(2)} \quad \text{O} = \text{O} + \text{CH}_3
\]

The main consumption pathway of $\beta$-scission of PODE$_2$ dehydrogenation radicals could be referred to DMM as follows:

\[
\text{(3)} \quad \text{O} = \text{O} + \text{O} = \text{O} + \text{O} + \text{CH}_3
\]

\[
\text{(4)} \quad \text{O} = \text{O} + \text{O} = \text{O} + \text{O} + \text{O}
\]

\[
\text{(5)} \quad \text{O} = \text{O} + \text{O} + \text{O} = \text{O} + \text{O} + \text{O}
\]

Reaction (3) and (1) were both $\beta$-scission reactions with methylene as the active site, so the same rate constant was used. In reactions (4) and (5), $\beta$-scission could be occurred in both directions at the same time, the rate constants similar to those of reactions (2) were used because the active sites of the reactions were similar. It should be noted that since the reaction class was heavily pressure dependent reaction, the inverse reaction rate constant of DMM should be derived from the thermodynamic data and the positive reaction rate, and then the inverse reaction rate constant should be analogized to PODE$_2$.

For the kinetic mechanism of PODE$_1$-$3$ developed in this paper, all the thermodynamic data of DMM species were derived from Jacobs model and the thermodynamic data of PODE$_2$ and PODE$_3$ species were derived from He model. The species of PODE$_2$ and PODE$_3$ not included in He model were calculated by THERM package based on the Group Additivity Theory of Benson.
### Table 1. PODE\(_n\) reaction classes of the model developed in this paper

| Number | Reaction class                                                                 | Reaction category         |
|--------|-----------------------------------------------------------------------------|---------------------------|
| 1      | Unimolecular decomposition of the fuel                                       | High temperature reactions|
| 2      | \(RH \rightleftharpoons \tilde{R} + \tilde{H}\)                            |                           |
| 3      | \(RH + X \rightleftharpoons \tilde{R} + XH\)                              |                           |
| 4      | \(\text{C-O: } \beta\text{-scission of } \tilde{R} \text{ radicals}\)        |                           |
| 5      | \(\text{O-C-O: } \beta\text{-scission of } \tilde{R} \text{ radicals}\)     |                           |
| 6      | \(\tilde{R}\) radical isomerization                                         |                           |
| 7      | \(\tilde{R} + O_2 \rightleftharpoons \tilde{R}O_2\)                       | Low temperature reactions |
| 8      | \(\tilde{R} + \text{R'}O_2 \rightleftharpoons \tilde{R}O + \text{R'}\tilde{O}\) |                           |
| 9      | \(\tilde{R}O_2 \rightleftharpoons \text{Q'O'OH}\)                         |                           |
| 10     | \(\text{R'O}_2 + \text{HO}_2 \rightleftharpoons \text{ROOH} + O_2\)       |                           |
| 11     | \(\text{R'O}_2 + \text{H}_2\text{O}_2 \rightleftharpoons \text{ROOH} + \text{HO}_2\) |                           |
| 12     | \(\text{R'O}_2 + \text{CH}_3\text{O}_2 \rightleftharpoons \text{RO} + \text{CH}_3\text{O} + O_2\) |                           |
| 13     | \(\text{R'O}_2 + \text{RO}_2 \rightleftharpoons \text{RO} + \text{RO} + O_2\) |                           |
| 14     | \(\text{ROOH} \rightleftharpoons \text{R}'O + \tilde{O}H\)                |                           |
| 15     | \(\tilde{R}'O\) decomposition                                             |                           |
| 16     | \(\text{Q'OOH} \rightleftharpoons \text{Q'O} + \tilde{O}H\) (cyclic ether formation) |                           |
| 17     | \(\text{Q'OOH} \) decomposition (\(\beta\)-scission products)             |                           |
| 18     | \(\text{Q'OOH} + O_2 \rightleftharpoons \text{O}_2\text{QOOH}\)          |                           |
| 19     | Isomerization of \(\text{O}_2\text{QOOH}\) and formation of ketohydroperoxide and \(\tilde{O}H\) |                           |
| 20     | Decomposition of ketohydroperoxide to form oxygenated radical species and \(\tilde{O}H\) |                           |
| 21     | Cyclic ether reactions with \(\tilde{O}H\) and \(\text{HO}_2\)             |                           |

3. Verification and discussion of PODE\(_n\) model

#### 3.1. Underlying DMM mechanism

The accuracy of DMM mechanism is particularly important because the reaction mechanism of PODE with high degree of polymerization is derived from DMM mechanism. The comparison of ignition delay of DMM under different chemical equivalence ratio and air dilution conditions was shown in Figure 1. The experimental data were from Hu and Jacobs, the solid line represented the predicted value of the model developed in this paper, the dotted line represented the predicted value of He model.

It can be observed from Figure 1 that the model developed in this paper showed reasonable prediction ability for ignition delay in a wide temperature range and a slightly higher prediction value under high temperature and low pressure conditions. The prediction values of He model under high pressure conditions were obviously higher than the experimental values, and the differences were more obvious under medium and low temperature conditions. This indicated that the DMM mechanism of He model underestimated the reactivity of fuel seriously, especially at the low and medium temperature condition. The comparison of the measured and calculated values of DMM concentration in JSR experiments was shown in Figure 2. It can be observed from Figure 2 that the model developed in this paper showed reasonable prediction ability for most species concentration but the predicted values for methanol (CH\(_3\)OH) concentration were inaccurate. The consumption rate of DMM fuel of He model was obviously faster, and the prediction values of important intermediate species such as methanal (CH\(_2\)O), methane (CH\(_4\)), methyl formate (CH\(_3\)OCHO) were seriously higher. This indicated that the prediction of reaction path during DMM oxidation process of He model was not accurate. In summary, the prediction ability of He model for the DMM experimental data in literature was insufficient, and the prediction ability of the model developed in this paper was reasonable for most experimental data.
3.2. Mechanism of PODE$_n$ with high degree of polymerization

At present, the kinetic experimental data of PODE$_n$ with high degree of polymerization are scarce. The comparisons of the experimental data and the simulated results of the model of PODE$_3$ ignition delay time were shown in Figure 3. The experimental data were from Hu, the solid line represented the simulated results of He model and the dotted line represented the simulated results of the model developed in this paper. As shown in the Figure 3, the predicted values of PODE$_3$ ignition delay time of He model were slightly higher than the measured values under all experimental conditions and the deviation increased with an increase of pressure. This was consistent with the prediction results of He model for ignition delay time of DMM. The predicted values of ignition delay time of the model developed in this paper showed good agreement with the measured value when the equivalence ratio was 0.5 while the predicted values were lower than the measured values when the equivalence ratio was 1.0 and 2.0. The changes of pressure had little influence on the prediction ability.

3.3. Discussion of reaction classes

The same modeling method was used in He model and the model developed in this paper and the thermodynamic data of PODE$_n$ with high degree of polymerization were almost the same. However, the simulation results of PODE$_n$ with different degree of polymerization showed opposite results. This may be that the simple analogy method was not appropriate in the modeling process. He calculated the DMM and PODE$_2$ reactions (reactions 1-5) for the β-scission reaction classes of fuel dehydrogenation radicals, as shown in Figure 4. Methanal was produced by reaction (1), reaction (3) and dimethyl ether (DME), and the reaction sites of free radicals were the same and the rate coefficients were very close. While the difference between reactions (4), (5) and reaction (2) was significant, for example, at the
condition of 600 K, the rate coefficients of reaction (5) were four times higher than that of reaction (2). The difference may be more obvious with the increase of degree of polymerization. Therefore, the same reaction classes of PODE\textsubscript{n} with different degree of polymerization may not have the same rate coefficient criterion.

In the process of modeling, the difference of rate coefficients between PODE\textsubscript{n} with different degree of polymerization in the same reaction class was not considered in He model and the model developed in this paper, and the same rate coefficient criterion (DMM rate coefficient) was adopted for the same reaction class. The rough treatment of this modeling method may lead to the opposite prediction results of the two models: the underlying DMM mechanism of He model was not accurate, but He model could forecast the experimental data of PODE\textsubscript{3} accurately; accurate and detailed DMM mechanism was adopted in the model developed in this paper, but the PODE\textsubscript{3} mechanism was not accurate. Therefore, the difference of rate coefficients among the internal mechanisms of important reactions had to be considered for developing more detailed and reliable PODE\textsubscript{n} mechanism with high degree of polymerization.

![Figure 4. Comparison of rate constants of partial reactions.](image)

### 4. Conclusion

(1) Compared with the existing PODE\textsubscript{n} model and experimental data, it was observed that He model could forecast the experimental data of PODE\textsubscript{3} accurately. However, previous model could not match the experimental data in ST and JSR of DMM and overestimated its chemistry reactivity in low to intermediate temperature range, which indicated that the prediction ability for DMM in previous model was poor.

(2) In this paper, a PODE\textsubscript{3} kinetic mechanism model was preliminarily developed based on accurate detailed DMM mechanism with same modeling method of He et al. The thermodynamic data of the species not included in He model were calculated by THERM package based on the Group Additivity Theory of Benson. The model developed in this paper could forecast DMM experimental data in ST and JSR accurately, but the predicted values of PODE\textsubscript{3} ignition delay time in RCM were lower than the measured values.

(3) The rate coefficients of the same reaction class of PODE\textsubscript{n} with different degree of polymerization showed great difference. The mechanism of PODE\textsubscript{n} with low degree of polymerization could not be directly extended to PODE\textsubscript{n} with higher degree of polymerization. The difference of rate coefficients among the internal mechanisms of important reactions had to be considered for developing more detailed and reliable PODE\textsubscript{n} mechanism with high degree of polymerization.
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