



Experimental and kinetic study on ignition delay times of dimethyl carbonate at high temperature



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HIGHLIGHTS

- Ignition delay times of dimethyl carbonate were measured in a shock tube for the first time at different conditions.
- A modified DMC kinetic model was proposed and can well predict ignition delay times and activation energies.
- DMC is primarily consumed through the H-abstractions and not fuel unimolecular decompositions for high temperature ignition.

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ABSTRACT

Ignition delay times of dimethyl carbonate were measured in a shock tube for the first time at $T = 1100\text{--}1600\text{ K}$, $p = 0.12\text{--}1.0\text{ MPa}$, fuel concentration = 0.5–2.0%, and $\phi = 0.5\text{--}2.0$. A modified chemical kinetic model was developed and can well predict ignition delay times and activation energies. Further validation of the proposed kinetic model was made on the basis of the opposed flow diffusion flame data. Reasonable agreements were also achieved under the literature data. Reaction pathway analysis shows that at high temperature the DMC molecule is primarily consumed through the H-abstractions but not fuel unimolecular decompositions. Sensitivity analysis provides some key fuel-species reactions for DMC high temperature ignition.

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1. Introduction

It has been proven that oxygenated fuels are effective in reducing soot emissions from diesel engines. Researches concerning engine performance and emissions have been conducted widely on diesel engines fueled with various oxygenates, such as alcohols, ethers, esters, carbonates and acetates [1–4]. As a promising oxygenated fuel, Dimethyl carbonate (DMC) possesses a very high percentage of oxygen. Engine studies indicated that the DMC addition to the diesel could efficaciously decrease the smoke emissions [5–7]. Previous studies revealed that the addition of ethers was more efficient in reducing the smoke emissions compared to the addition of alcohols [8], and that dimethyl carbonate was even more efficient than other ethers [7]. However, there are numerous simultaneous processes in the engine which make it difficult to determine the mechanism for such decrease.

Little work has been published regarding fundamental combustion researches of DMC in recent years. Sinha and Thomson [9] measured the species and temperatures in an opposed flow diffusion flames of iso-propanol, dimethoxy methane (DMM), and dimethyl carbonate (DMC). For DMM and DMC, the absence of C–C bonds effectively decreases the formation of soot precursors such as ethylene, acetylene, and propylene. Compared to the propane flame, the ethylene levels of iso-propanol, DMM, and DMC flames were reduced by 41%, 77%, and 93%, respectively. However, their work did not cover the development of chemical kinetic model. Sinha and Thomson [9] studied the experimental species profiles by experimenting in an opposed flow diffusion flame and it gave the exclusive validation of the only available DMC kinetic model [10], which is developed by Glaude and can well simulate the DMM and DMC diffusion flame results. This model was also compared with species profiles obtained in premixed low-pressure (30 Torr) flames of heptane with DMC addition, and an overall satisfactory agreement was attained by Chen et al. [11]. Badin measured the laminar flame speed using the heat flux method, but Glaude DMC model significantly overpredicted the experimental values [12].

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In fact, many reaction rate constants in this DMC model were determined by estimation. Further development and validation of the DMC kinetic model are lagging due to the lack of more accurate fundamental experimental data. For instance, there are not reported ignition delay time data yet.

Therefore, the objectives of the present work include the measurement the ignition delay time of DMC under different conditions, the validation of the DMC chemical kinetic model, and the interpretation of the ignition chemistry through reaction pathway and sensitivity analysis.

2. Experimental and calculated approach

Ignition delay times were measured in a shock tube and the detailed description of the experimental apparatus can be referred to the previous publications [13,14]. The time interval between the arrival of incident shock wave at the endwall and the intercept of the maximum slope of the CH^* trajectory with the zero line is defined as the measured ignition delay time (τ) in the current study. Ignition temperatures (T) are calculated with Gaseq [15]. The tested ranges of the equivalence ratio and the pressure of DMC/oxygen/argon mixtures were 0.5–2.0 and 0.12–1.0 MPa, respectively. The respective purities of DMC, oxygen and argon are 99.9%, 99.999% and 99.9999%. Table 1 shows the compositions of test mixtures in detail.

Calculations were carried out using Chemkin [16] and Senkin [17] codes and applying the constant volume adiabatic model. The maximum increase rate of temperature profile ($\max dT/dt$) is used to define the calculated ignition delay time in this study.

3. Chemical kinetic model

The unique DMC chemical model available at present was developed by Glaude in 2005 [10]. It consists of the C1–C3 model developed by Curran and the DMC sub-model developed by Glaude. Although this model was validated with DMC opposed-flow diffusion flames [10], it cannot give a satisfactory prediction to the experimentally measured ignition delay times of this study.

The modified chemical kinetic model in this study was enhanced by adding the DMC sub-model to Aramco Mech 1.3 model [18] and it consists of 275 species and 1586 reactions as a whole. DMC sub-model consists of 24 elementary reactions absorbing the Glaude DMC sub-model [10] and Dooley MB sub-model [19]. Detailed mechanism including thermochemical data is given in Supporting Information. It can be observed that the modification was mainly conducted on the DMC sub-model, while the original C4 chemistry remained the same. Table 2 [10,19–23] provides further details of the modified DMC sub-model.

3.1. Unimolecular decomposition

Fig. 1 gives the bond dissociation energies of dimethyl carbonate, methyl butanoate and dimethyl ether [24]. The bond energies of $\text{CH}_3\text{OC}^*\text{OO}-\text{CH}_3$ (374.5 kJ/mol) and $\text{CH}_3\text{OC}^*\text{O}-\text{OCH}_3$ (427.2 kJ/mol) in DMC are different and they are also unequal to that of

$\text{CH}_3\text{O}-\text{CH}_3$ (351.5 kJ/mol). Therefore, in Glaude DMC model [10], it is improper to adopt the rate constant of $\text{CH}_3\text{O}-\text{CH}_3$ decomposition reaction as that of R1565 and R1566.

Bond energies of $\text{CH}_3\text{OC}^*\text{OO}-\text{CH}_3$ (374.5 kJ/mol) and $\text{CH}_3\text{OC}^*\text{O}-\text{OCH}_3$ (427.2 kJ/mol) in DMC are almost identical to those of $\text{C}_3\text{H}_7-\text{C}^*\text{OO}-\text{CH}_3$ (364.1 kJ/mol) and $\text{C}_3\text{H}_7\text{C}^*\text{O}-\text{OCH}_3$ (423.9 kJ/mol) in methyl butanoate. On the basis of analogical method, the reaction rates of these two bond fission should have the same values at the same temperature. As a result, the rate constants of $\text{CH}_3\text{OC}^*\text{OO}-\text{CH}_3$ (R1565) and $\text{CH}_3\text{OC}^*\text{O}-\text{OCH}_3$ (R1566) decomposition, recommended by Dooley et al. [19] for the decompositions of methyl butanoate, were adopted in the present model.

It is reported by Glaude [10] that R1567 is a new molecular elimination path for the DMC and the activation energy of this elementary reaction was determined by CBS-Q plus corrections with isodesmic reactions. The present model employed the rate constant of R1567 of Glaude's calculation. R1568 is another DMC unimolecular decomposition reaction, and its rate constant was determined by Glaude's estimation [10,20].

3.2. Hydrogen abstraction

It was proved that H-abstraction is the main pathway for the consumption of typical fuels at high temperature ignition [14,25,26]. In Glaude DMC model, the rate constants of H-abstraction by radicals (R1573, R1575 and R1577) are assumed to that of the secondary C–H of *iso*-octane. Analogism can be made between the other H-abstraction reactions and the primary and secondary C–H of *n*-heptane. Fig. 2 gives the bond dissociation energies in Glaude DMC model of *n*-heptane and *iso*-octane at 298 K [24]. The bond dissociation energy of C–H in DMC molecule (422.6 kJ/mol) is different to that of *n*-heptane (367.8 kJ/mol and 409.6 kJ/mol) and *iso*-octane (399.6 kJ/mol), but it is close to that of primary C–H (414.2 kJ/mol) in methyl butanoate. Therefore, the present model assumed the rate constants of H-abstraction reactions of DMC to be identical to that of methyl butanoate.

3.3. Ether-acid conversion

R1579 is another consumption pathway of DMC molecule producing the COC^*OOH . Since this reaction has small branching ratio and consequently has little effect on the ignition delay time, the rate constant of this elementary reaction was also adopted by Glaude's estimation [10].

3.4. Hydrogen abstraction of COC^*OOH

COC^*OOH is mainly consumed by hydrogen abstraction with small radicals (R1580–R1583). These reactions are also taken from the Glaude's estimation [10].

3.5. Radical decomposition

CJOC^*OOH radical is the product of hydrogen abstraction of COC^*OOH , and it decomposes to CH_2O , CO and OH through R1584. COC^*OOJ radical, the product of R1565, produces CH_3O and CO_2 . COC^*COOCJ radical is the main product of DMC molecule consumption, decomposing CH_3OCO and CO_2 . These three rate constants (R1584–R1586) were assumed by Glaude [10].

Decomposition of the CH_3OCO radical has been the subject of recent attention [10,27]. In this model, we employed Glaude's expression of CH_3OCO decomposition calculated by CBS-Q method, which has been validated with speciation data of an opposed flow diffusion flame in his modeling study. The model prediction indicates the importance of the decomposition of CH_3OCO , because its productions – CO_2 and CH_3 radicals – dominate free radical

Table 1
Composition of DMC–O₂–Ar mixtures.

Mixtures	ϕ	X_{DMC} (%)	X_{O_2} (%)	X_{Ar} (%)	p (MPa)
6	0.5	1.0	6.0	93.0	0.12, 0.5, 1.0
7	1.0	1.0	3.0	96.0	0.12, 0.5, 1.0
8	2.0	1.0	1.5	97.5	0.12, 0.5, 1.0
9	1.0	0.5	1.5	98.0	0.5
10	1.0	1.5	4.5	94.0	0.5
11	1.0	2.0	6.0	92.0	0.5

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