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An experimental and modeling study of the ignition of dimethyl carbonate in shock tubes and rapid compression machine

Katiuska Alexandrino[a,b,*], María U. Alzueta[b], Henry J. Curran[a]

[a] Combustion Chemistry Centre, School of Chemistry, National University of Galway, Galway, Ireland
[b] Aragón Institute of Engineering Research (I3A), Department of Chemical and Environmental Engineering, University of Zaragoza, 50018 Zaragoza, Spain

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ABSTRACT

Ignition delay times of dimethyl carbonate DMC were measured using low- and high-pressure shock tubes and in a rapid compression machine (RCM). In this way, the effect of fuel concentration (0.75% and 1.75%), pressure (2.0, 20, and 40 atm) and equivalence ratio (0.5, 1.0, 2.0) on ignition delay times was studied experimentally and computationally using a chemical kinetic model. Experiments cover the temperature range of 795–1585 K. Several models from the literature were used to perform simulations, thus their performances to predict the present experimental data was examined. Furthermore, the effect of the thermodynamic data of the $CH_3O(C{=}O)\dot{O}$ radical species and the fuel consumption reaction $CH_3O(C{=}O)OCH_3 \rightleftarrows CH_3O(C{=}O)\dot{O} + \dot{C}H_3$, on the simulations of the ignition delay times of DMC was analyzed using the different models. Reaction path and sensitivity analyses were carried out with a final recommended model to present an in-depth analysis of the oxidation of DMC under the different conditions studied. The final model uses AramcoMech 2.0 as the base mechanism and includes a DMC sub-mechanism available in the literature in which the reaction $CH_3O(C{=}O)OCH_3 \rightleftarrows CH_3O(C{=}O)\dot{O} + \dot{C}H_3$ has been modified. Good agreement is observed between calculated and experimental data. The model was also validated using available experimental data from flow reactors and opposed flow diffusion and laminar premixed flame studies showing an overall good performance.

1. Introduction

Dimethyl carbonate ($CH_3O(C{=}O)OCH_3$, DMC), a non-toxic and non-corrosive carbonate ester with no C–C bonds and containing 53% oxygen by weight, has been identified as a suitable fuel compound to be added to diesel fuel to reduce PM emissions without affecting NO_X emissions [e.g., 1]. Even though it is 100% miscible with diesel fuel, it must be used as a blended fuel in diesel engines due to its low cetane number (35–36), low calorific value (15.78 MJ/kg), and high latent heat of evaporation (369 kJ/kg) [2,3].

To contribute to the development of detailed chemical kinetic models to describe the combustion characteristics of DMC, a thorough understanding of its combustion chemistry is needed. These chemical kinetic models can be used in conjunction with computational fluid dynamics (CFD) codes, with the necessary simplifications, to simulate the physical and chemical processes in engines, leading to optimal engine efficiency with minimal emissions. To this end, studies addressing the thermal decomposition [4–6], photolysis [7] and oxidation of DMC have been reported in the literature.

Sinha and Thomson [8] measured species concentrations across DMC/air and propane/DMC/air opposed flow diffusion flames. Formaldehyde was found to be an important intermediate species in the DMC flame, and the presence of oxygen on the central carbon in DMC favors breakage of the O–CO bond which results in very low levels of formation of methane, ethane, ethylene, and acetylene. Glaude et al. [9] developed the first chemical kinetic sub-mechanism for DMC conversion, which was incorporated into a previously developed chemical kinetic mechanism for dimethoxy methane (DMM) and dimethyl ether (DME) [10,11]. The predicted composition profiles using this model were in reasonable agreement with the measured species profiles from Sinha and Thomson [8].

Chen et al. [12] investigated the oxidation of n-heptane/DMC/O_2/Ar mixtures in a laminar pre-mixed low-pressure (30 Torr) flame, at an equivalence ratio of 1.16, using synchrotron photoionization and molecular-beam mass spectrometry (PI-MBMS) techniques. Measured and simulated mole fraction profiles of major and intermediate species were compared. The

* Corresponding author at: Aragón Institute of Engineering Research (I3A), Department of Chemical and Environmental Engineering, University of Zaragoza, C/ Mariano Esquillor, s/n, 50018 Zaragoza, Spain.
E-mail address: katyalex@unizar.es (K. Alexandrino).

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calculations were performed using a model which includes the DMM and DMC sub-mechanisms from the model developed by Glaude et al. [9]. The predicted concentrations of flame species agree reasonably well with the measured results. The authors observed an early production of CO_2 in both the measured and modeling results which is suggested to occur mainly due to the decomposition of methoxy formyl ($CH_3O\dot{C}{=}O$) radicals.

Peukert et al. [13,14] studied the high temperature thermal decomposition of DMC, and its interaction with $\dot{H}$ and $\ddot{O}$ atoms, using the shock tube technique in conjunction with master equation analysis. Bardin et al. [15] measured laminar burning velocities of DMC/air flames at initial gas mixture temperatures of 298, 318, 338, and 358 K. These results were simulated using the model developed by Glaude et al. [9], and it was found that the model significantly over-predicted the measured laminar burning velocities.

More recently, Hu et al. [16] measured ignition delay times of DMC oxidation in a shock tube at high temperatures (1100–1600 K), at different pressures (1.2–10 atm), fuel concentrations (0.5–2.0%) and equivalence ratios ($\varphi = 0.5$–2.0). A chemical kinetic model, based on the modification of the DMC sub-mechanism from Glaude et al. [9] and the AramcoMech 1.3 mechanism [17], was proposed to describe the ignition delay times of DMC. The measured ignition delay times from this work, as well as the DMC/air opposed diffusion flame data reported by Sinha and Thomson [8], were compared with model calculations showing good agreement.

Sun et al. [18] investigated both pyrolysis of DMC in a flow reactor at different pressures (40, 200 and 1040 mbar) and its oxidation in laminar premixed low-pressure DMC/O_2/Ar flames at equivalence ratios of 1.0 and 1.5, at 25 and 30 Torr, respectively. A detailed kinetic model for DMC pyrolysis and combustion, based on a new sub-mechanism for DMC conversion and the AramcoMech 1.3 mechanism [17], was proposed. This model was validated using the experimental data obtained by Sun et al. [18] and with the opposed flow flame [8], burning velocities [15] and shock tube [16] experimental data from the literature. A more detailed description of these three DMC sub-mechanisms [9,16,18] is further shown in Section 3.

Most recently, Alzueta et al. [19] carried out an atmospheric flow reactor study of DMC oxidation in the absence and presence of NO in the temperature range 700–400 K at $\varphi = 0.028$, 1.0, 1.43, and 3.33. It was found that, in the DMC–NO interaction, the fuel-rich conditions contribute slightly to the net reduction of NO_x. A detailed kinetic model, based on the DMC sub-mechanism from Glaude et al. [9] and a core mechanism described and updated by the authors [20–24], was proposed. With this model, these authors evaluated the impact of the thermodynamic data on the modeling results, finding that the enthalpy of formation of the DMC radical $CH_3O(C{=}O)\dot{O}$ significantly influences the DMC conversion results. The influence of the thermodynamics of the $CH_3O(C{=}O)\dot{O}$ radicals species on our current ignition delay time measurements will be further discussed in Section 4. Alzueta et al. [19] also performed one DMC pyrolysis experiment in an atmospheric flow reactor in order to determine its capacity to form soot, which was found to be very low. Following this work, Alexandrino et al. [25] studied the sooting propensity of DMC through pyrolysis experiments in an atmospheric flow reactor in the temperature range 1075–1475 K and inlet DMC concentrations of 33,333 and 50,000 ppm. It was confirmed that DMC has a very low tendency to form soot, even when compared with ethanol, because the formation of CO and CO_2 is favored, and thus few carbon atoms are available for soot formation. The formation of CO_2 is highly favored by the decomposition of the $CH_3O\dot{C}{=}O$ and $CH_3O(C{=}O)\dot{O}$ radicals. Soot reactivity and characterization by instrumental techniques was also considered, showing that the higher the temperature and the inlet DMC concentration of soot formation, the lower the reactivity of the soot.

Table 1
Composition of DMC mixtures studied in the low-pressure shock tube.

Mix.	P_5[a] (atm)	φ	DMC (mole%)	O_2 (mole%)	Ar (mole%)
1A	2.0	0.5	0.75	4.5	94.75
2A	2.0	1.0	0.75	2.25	97.0
3A	2.0	2.0	0.75	1.12	98.12
4A	2.0	0.5	1.75	10.5	87.75
5A	2.0	1.0	1.75	5.25	93.0
6A	2.0	2.0	1.75	2.62	95.62

[a] P_5 is the pressure behind the reflected shock wave.

To our knowledge, to date the work of Hu et al. [16] is unique in studying ignition delay times for DMC oxidation. Although that work covered a wide range of equivalence ratios, DMC concentrations and pressures, more experimental data for the ignition of DMC are needed to develop and validate chemical kinetic models to accurately describe DMC combustion. Keeping this in mind, the aims of this work are: 1) to study ignition delay times of DMC under new experimental conditions, and thereby extend the available experimental data of DMC oxidation. In particular, low- and high-pressure shock tubes were used and, for the first time, a rapid compression machine was used in order to extend the high-pressure shock tube data of DMC to lower temperatures; 2) to compare the performance of the different models for DMC conversion available in the literature to predict the measured ignition delay times of this work. This also includes the analysis of the effect of changing the thermodynamic of the $CH_3O(C{=}O)\dot{O}$ radicals species and reaction kinetics on the modeling calculations. The goal is to find a model that best predicts our experimental ignition delay times and also various other experimental targets including flow reactors and opposed flow diffusion and laminar premixed flames; and 3) to perform the chemical interpretation of the effect of the DMC concentration, pressure and equivalence ratio on measured ignition delay times through rate of production and sensitivity analyses.

2. Experimental

Shock tube and rapid compression machine ignition delay time data were obtained using the facilities at the National University of Ireland Galway (NUIG). The full list of mixtures studied and their compositions are provided in Tables 1 and 2. Experiments with stoichiometric and fuel-rich mixtures compressed at 40 atm could not be performed in the rapid compression machine due to the high rate of heat release during ignition, which damaged the pressure transducer used to monitor the pressure.

DMC liquid (99% pure, Sigma-Aldrich) was used without further purification. O_2, Ar and N_2 cylinders were supplied by BOC at high purity (99.5%). Mixtures were prepared in an evacuated and heated (348 K) stainless steel mixing tank at each facility, using the partial pressure method. The fuel was injected via an injection port on the tank using a gas-tight syringe, followed by the addition of O_2 and finally the diluent (Ar or N_2). For all conditions, the partial pressure of the fuel was maintained at a value less than one-third that of its saturated vapour pressure at the tank temperature to avoid fuel condensation. Each mixture was allowed to homogenize overnight before use. The uncertainty in mixture concentrations is estimated to be ±2%. The experimental procedure and facilities to determine the ignition delay time data are explained briefly below.

2.1. Low-pressure shock tube

To measure the ignition delay time of DMC/O_2/Ar mixtures at high temperatures ($T = 1220$–1585 K) and at low pressure ($P = 2.0$